A DISSERTATION ON

STUDIES ON THE BIOLOGICAL OXIDATION OF THIOSULPHATE USING COMPLETE MIX REACTORS WITHOUT RECYCLE

by

PETER JONATHAN PAINE

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Department of Civil Engineering
School of Graduate Studies
University of Ottawa
Ottawa, Canada

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Peter Jonathan Paine
University of Ottawa
Ottawa, Ontario
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ABSTRACT

Discharge of partially oxidized sulphur compounds called thiosalts (formed during grinding and flotation operations) at neutral or alkaline pH values from tailings ponds, has resulted in acidic conditions (pH 2.5 ∿ 3.5) in receiving streams.

The problem has been attributed to the biological oxidation of these thiosalts, by sulphur-oxidizing bacteria of the Thiobacillus species, prevalent in the receiving streams.

Treatment consists of either a biological or chemical oxidation of the thiosalts, the main constituent of which is thiosulphate, to sulphuric acid, followed by neutralization before final discharge. Economic considerations dictate largely the mode of oxidation used.

This report had as its purpose the investigation of the phosphorus requirements of a biological oxidation process and the determination of a minimum retention time capable of facilitating a satisfactory thiosalt oxidation.

Experiments for both investigations were conducted in completely mixed reactors without recycle, simulating an aerated lagoon. A synthetically prepared thiosulphate solution of uniform concentration supplemented with nutrients (N,P) and trace elements served as the influent.

Results of the phosphorus requirement investigation showed that an influent phosphorus concentration of 2.96 mg/l PO_4-P and a retention time of 5 days were sufficient to achieve thiosulphate removals exceeding 99 percent.

Results of the retention time investigation showed that a retention time of one day at an influent phosphorous concentration of 9.80 mg/l PO_4-P was sufficient for thiosulphate removals exceeding 99 percent.

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CHAPTER 1

INTRODUCTION

One of the many factors responsible for Canada's wealth is the mining of fortuitous deposits of various bodies of ore formed many years ago as the earths outer mantle cooled. Subsequent mining and exporting of this ore has sustained an industrial base upon which social and economic development has been and is made possible, and the mining industries in Canada continue to play an important role in the development of this country.

The range and economic significance of the mining industry in Canada is shown in Table 1, which is a selection of production statistics for some base metals - the figures were obtained from the Canada Minerals Yearbook, 1975 (6).

The base metal mining industry, however, is not entirely free from environmental problems, and the source of waterborne contaminant arising from base metal mining operations can be classified into two distinct types.

(i) acids generated from the atmospheric exposure of metallic sulphide ores, during and after mining operations

and

(ii) contaminants arising from the processing of the ore.

The origin of both types of problems appear to be related to the high sulphide content of the ores from which the metals are

TABLE 1

PRODUCTION STATISTICS FOR SOME BASE METALS

after Canadian Minerals Yearbook - 1975 (6)

METAL	TOTAL PRODUCTION (tons)*	REVENUE FROM PRODUCTION (dollars)	TOTAL EXPORTS (tons*)	REVENUE FROM EXPORTS (dollars)
Copper	798,132	1,016,819,000	783,878	835,520,000
Zinc	1,193,809	895,537,000	1,086,277	506,904,000
Lead	373,065	151,837,000	-	105,561,000
Nickel	299,661**	977,681,000	293,880**	872,416,000

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[*] The short ton of 2000 pounds is used throughout, unless otherwise indicated.

[**] Long tons (one long ton = 2240 pounds).

extracted. Examples of some sulphidic ores are pyrite (FeS_2), galena (PbS), sphalerite (ZnS), molybdenite (MoS_2), millerite (NiS), and covellite (CuS).

The former of the two environmental problems, termed mine acid drainage, is the result of chemical or biological oxidation of the ores. Evidence favours the biological mechanism, with the bacterium *Thiobacillus ferrooxidans* being responsible. Table 2 presents a summary of relevant chemical equations involved in the biological oxidation.

Potential types of pollutants associated with this type of wastewater, if not collected and treated, are an acidic pH and a high heavy metals content (Cu, Zn, Pb, Ni, Fe). (Acid generation contributes to the leaching of heavy metals from abandoned mines). Table 3 is a typical assay of acid waters in Canada.

Treatment, for this wastewater, consists of acid neutralization and subsequent precipitation of the heavy metal as an insoluble hydroxide. This is an established and standard treatment procedure for heavy metals removal.

The latter type of pollutant, contaminants arising from the processing of the ores, is generated during the milling and flotation operations where, due to the nature of milling and chemicals employed in flotation, the net result is the formation of thiosulphate ($S_2O_3^{2-}$) and other unoxidized sulphur compounds, known as polythionates. (Thiosulphate and the polythionates are collectively known as thiosalts).

The thiosalts are unstable and are converted biologically by

TABLE 2

EQUATIONS INVOLVED IN THE BIOLOGICAL GENERATION OF MINE ACID DRAINAGE, after Schmidt & Conn (23)

---

(1) $2FeS_2 + 7O_2 + 2H_2O \rightarrow 2FeSO_4 + 2H_2SO_4$ (pyrite)

(2) $4FeSO_4 + H_2SO_4 + O_2 \rightarrow 2Fe_2(SO_4)_3 + 2H_2O$
(in the presence of *T. ferrooxidans*)

(3) $Fe_2(SO_4)_3 + 6H_2O \rightarrow 2Fe(OH)_3 + 3H_2SO_4$

(4) $Fe_2(SO_4)_3 + FeS_2 + H_2O \rightarrow 3FeSO_4 + 2S$

(5) $S + 3O + H_2O \rightarrow H_2SO_4$
(in the presence of *T. thiooxidans*)

(6) $FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$

TABLE 3

TYPICAL ASSAYS OF ACID WATERS IN CANADA

(All Concentrations are mg/l except pH), after Scott and Bragg (24)

Type of Operation	Cu-Pb-Zn (Mine & Surface Drainage)	Cu-Pb-Zn (Mine Water)	Uranium (Seepage)	Cu-Zn (Active Mine)	Base Metal (Abandoned)	Uranium (Abandoned Mine)
pH	4.0	2.0	2.0	3.0	2.6	2.0-2.8
Suspended Solids	8.8	690	Nil	-	-	25
Total less solids	79	24,000	-	-	9,200	13,440
Hardness	293	2,960	-	-	1,390	
Ca	-	-	4.6	-	454	-
Mg	-	-	106	-	178	-
Cu	17	11	3.6	0.0	2.5	2.2
Zn	118	1,090	11.4	0.4	34	9.4
Pb	0.4	58	0.7	0.11	0.5	-
Fe (total)	79	1,830	3,200	11.7	1,300	300
Mn	21	0	5.6	0.4	8.2	3.6
SO_4	36	16,560	7,440	885	4,050	6,900
COD	-	245	270	-	110	-

various Thiobacillus species (especially Thiobacillus thiooxidans) to sulphate and hydrogen ions with subsequent pH depression (to pH 2.5-3.5) in the receiving body of water. Resulting environmental effects as a consequence of these low pH values include benthal damage and plankton,inverterbrate and, inevitably, fish kills. EIFAC (10) report that the safe pH range for fish is from pH 5-9, and that for maximum productivity the pH value should range between pH 6.5 and 8.5. These criteria have been widely quoted and the safe range of pH 5-9 has been generally accepted and adopted.

Economic losses usually follow from aquatic damage and fish kills. In a report on the Northeastern New Brunswick Mine Water Quality programme, Montreal Engineering Company Limited (19), discussing the value and potential of salmon resources in that province, state:

> "Estimates of the economic value of the Atlantic salmon resource in Northeastern New Brunswick are at best only a partial measure of its real value to society. The resource has no substitute and Canadians increasingly recognize it to be an itegral and significant part of their heritage."

Considerations, also, of the importance of the Atlantic salmon to Canada's international image should not be underestimated. A seven-country survey of foreign travel agents (19) showed the combination of hunting and fishing as the main reason for attracting more travel to Canada, and in 1969, Canada was one of the four countries with both travel receipts and expenditures in excess of $1 billion.

An estimation on the net value of the sport fishery to New Brunswick is given as between $4.6 million and $13.6 million. The Canada Department of the Environment estimates the gross expenditure by anglers in the province at $7,955,000. As these figures were for 1972, it is thought that they are now significantly greater in 1977.

Possible treatment for the unoxidized sulphur compounds consists of chemical and biological oxidation to sulphate, and subsequent neutralization of the acid produced, before discharge, or by the addition of a buffer in the effluent from the milling plant, to counteract acid generation, from thiosulphate oxidation, in the receiving stream. Costs dictate the choice of oxidant (O_2, Cl_2, OCl) used in chemical oxidation, and the concept of applying chemical treatment in the receiving stream is not encouraged, according to Scott and Bragg (24).

Thus, the accpeted mode of treatment of the thiosalts is by biological oxidation, using the appropriate species of Thiobacilli capable of thiosulphate oxidation. Although Thiobacilli are autotrophic organisms, and are capable of converting thiosulphate to sulphate, not all have the ability of converting thiosulphate to sulphate at rates fast enough to be applied in engineering design. The two most widely used species, having this ability, are T. thiooxidans and T. thioparus, the former operating at an optimum pH of 2.5-3.0 and the latter at a pH of 6.5-7.0. Table 4 summarizes various characteristics of the Thiobacilli.

Optimum conditions for biological oxidation, using T. thiooxidans,

TABLE 4

CHARACTERISTICS OF THE THIOBACILLI

after Schmidt (22)

Name	Substrates Utilized Other than Thiosulphate	pH Characteristics	Remarks
T. thiooxidans	Sulphur Tetrathionate	Optimum pH 2.0 to 3.0 Range 1.0 to 6.0	Acidophilic; oxidizes thiosulphate rapidly to sulphate.
T. ferrooxidans	Ferrous iron Sulphur Trithionate Tetrathionate	Optimum pH near 3.5 Range 2 to 6	Acidophilic; unable to use sulphur rapidly. Optimum pH for oxidation of sulphur compounds is apparently pH 4 to 5.
T. concretivorus	Similar to T. thiooxidans but differs principally in that it can use both ammonia and nitrate.		
T. thioparus	Sulphur Trithionate Tetrathionate Dithionate	Optimum pH near neutrality	Oxidation of substrate causes the medium to become acid.
T. denitrificans	Sulphur	Optimum pH near neutrality	Under anaerobic conditions uses nitrate as a terminal respiratory electron acceptor.
	Cultivated aerobically this bacterium is indistinguishable from T. thioparus.		
T. thiocyanoxidans	Thiocyanate Sulphur Sulphide	Optimum pH near neutrality pH 6.8 to 7.6	Produces acid, oxidizes thiosulphate rapidly.
T. novellus	Various organics	Optimum pH near neutrality	Grows slowly, produces acid. Of all the above thiobacilli this is not an obligate autotroph but a facultative autotroph.

Note: All the thiobacilli oxidize thiosulphate to sulphate although the precise pathways have not yet been agreed upon.

are a pH of 3.5, a temperature of 35°C, an adequate oxygen supply and nutrients. Completely mixed reactors (suspended growth systems) with and without recycle and fixed film growth reactors are capable of providing these conditions, and both systems have been used in practice.

The purpose of this report is to investigate the biological oxidation of thiosulphate using a completely mixed reactor (suspended growth) without recycle, with a view to determine, specifically:

(i) the effect of phosphorus (as inorganic phosphate) on the biological oxidation of thiosulphate;

and

(ii) the effect of solids retention time on the biological oxidation of thiosulphate.

CHAPTER 2

BACKGROUND

2.1 Initial Observations

The problem of acid generation from mining areas due to the oxidation of sulphidic minerals, chiefly pyrite (FeS_2), is a familiar one, and it has been extensively investigated and well documented. However, the same cannot be said for another environmental problem, namely unoxidized sulphur compounds, appearing in the effluent from milling processes.

The Fisheries Research Board of Canada, according to Schmidt and Conn (23), investigating this problem in October 1966 and July 1967 in New Brunswick, concluded that "one of several types of iron oxidizing bacteria were active in the formation of acid in the stream.

The British Columbia Research Council (ibid.), carrying out an investigation in November 1967 of a portion of the stream from the tailings pond to a point 5 miles downstream, concluded that the precipitation of calcium carbonate caused the observed decrease in pH and postulated that oxidation of ferrous iron by the bacterium Thiobacillus ferrooxidans, could produce acidic conditions in the stream.

In October 1968, Schmidt and Conn (23) of the Department of Energy, Mines and Resources, Government of Canada carried out a detailed investigation of the problem in New Brunswick, when it was observed that, regardless of the pH of the effluent from the tailings pond system, which varied from pH 9.0 in winter to pH 6.0 in summer, acidic conditions (pH 2.5 to 3.5) were produced in the receiving stream within a distance of 13 miles.

Their results show a pH decrease across both the tailings pond system (a total of 6 ponds) and from the discharge point of the tailings ponds to points downstream in the receiving stream. Additional analysis confirmed the presence of thiosulphate (about 1 g/l), various thionates (tri-, tetra-, and penta-) formed as the thiosulphate gradually disappeared, and sulphate the final state of thiosulphate oxidation.

Total sulphate (after oxidation) decreased from 3440 mg/l at the tailings discharge, where the pH was 11.7, to 1340 mg/l at a point 13.1 miles downstream, where the pH was 3.0. At this same point, sulphate was 1310 mg/l, showing a closeness between sulphate and total sulphate. Oxidation of partially oxidized sulphur compounds caused the pH depression in the receiving stream. Culturing studies also indicated the presence of the bacterium T. ferrooxidans.

Thus, Schmidt and Conn conclude that the mechanism of acid generation in the receiving stream is due to the oxidation of unoxidized sulphur compounds by T. ferrooxidans.

2.2 Formation of Unoxidized Sulphur Compounds

Unlike the formation of mine acid drainage, which is an ongoing process once a sulphide ore is exposed to the atmosphere and moisture, the formation of unoxidized sulphur compounds, thiosulphate and polythionates, is strictly related to the procedures involved in the extraction of the metals from the sulphidic ores in which they occur. This problem of unoxidized sulphur compounds is common to operations where sulphide ores are mined, milled and, eventually refined.

2.2.1 Mining and Milling Processes

Having mined the ore from the ground, the next step is extraction of valuable metals from the ore and separation of them from the gangue minerals (valueless minerals associated with ore minerals). This is facilitated by a process called beneficiation, also known as ore preparation and ore dressing.

In beneficiation, the minerals are broken apart by comminution (crushing, grinding, milling) and then subjected to concentration to produce one or more separate concentrates containing most of the ore minerals, and a discards or tailings containing most of the gangue minerals.

Before concentration, however, the ore is crushed; primary crushers reduce the ore to 4-6 inches in diameter (10-15 cm); secondary crushers further reduce this to about 3/4 inch diameter (2 cm). After crushing, the ore is milled to a particle size of about 1/100 of an inch (0.025 cm), with the final size of the particle related to the method of concentration to be used and the ore characteristics.

The next stage is to concentrate the separate sulphide minerals; differential flotation is used to accomplish this. Here, ore pulp (a mixture of ore pulp and water) is agitated in a mechanical flotation cell and air is drawn through the pulp. Flotable materials remain in the laden froth and the nonflotable material is passed to another flotation cell where flotation under different conditions may occur to concentrate other minerals.

It is during the process of comminution and concentration that formation of the unoxidized sulphur compounds occur.

2.2.2 Grinding Operations

During grinding and flotation operations in the sulphide milling concentrator, a small amount of sulphur from the minerals dissolves in the water. This process seems to be independent of water temperature but is known to accelerate in alkaline solutions normally used in some milling operations. In one particular operation, the water leaving a typical mill has a chemical oxygen demand (COD) of approximately 50 mg/l. This is not particularly high, but the products of oxidation with a passage of time generated sulphuric acid which caused the pH value of the soft receiving water to decrease to approximately 3.0. The sulphide conversion to thiosulfate in the mill circuit is described in the following equations, for pyrite, according to Uko (29):

$$FeS_2 + 2OH^- \rightarrow FeS + S^{2-} + H_2O + 1/2\ O_2 \qquad (1)$$

$$2S^{2-} + 2O_2 + H_2O \rightarrow S_2O_3^{2-} + 2OH^- \qquad (2)$$

Similarly, when pyrrhotite predominates in the ore, the following reaction may occur:

$$Fe_7S_8 + 2OH^- \rightarrow 7FeS + S^{2-} + H_2O + 1/2\ O_2 \qquad (3)$$

which is followed by reaction (2).

The following, also from Uko (ibid.), is an attempt to explain how a mixture of sulphur-oxygen compounds (the unoxidized sulphur compounds) can be produced in the grinding and flotation circuits.

Presumably, some of the sulphur is sheared off the ore in elemental form which, in ambient conditions, exists as a staggered eight member molecular ring.

$$8FeS_2 \rightarrow 8FeS + S_8 \qquad (4)$$

The free sulphur reacts with the sulphite ion which is produced in solution by dissociation in accordance with the reaction:

$$H^+ + S_2O_3^{2-} \rightarrow HSO_3^- + S \qquad (5)$$

and the combination of free sulphur and sulphite produce:

$$S_8 + HSO_3^- \rightarrow HS_9O_3^- \qquad (6)$$

This product is a linear molecule of sulphur-sulphur multiple bonds which is highly assymetrical and open to further S_N^2 attack by the HSO_3^- ion acting as a nucleophile

$$HSO_3^- + HS_9O_3^- \rightarrow HS_2O_3^- + HS_8O_3^- \qquad (7)$$

This reaction repeats itself and the resulting solution will contain a series of linear molecules such as $S_3O_6^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$, which are termed generally as polythionates.

Polythionates could also be created through the incomplete oxidation of iron sulphide minerals, Scott and Bragg (24), and according to Graham (11), thiosulphate is a constituent of the ammonical effluents which are produced by conventional coal carbonizing systems, and is formed largely by the oxidation of sulphide during the process of gas purification.

2.2.3 Flotation Operations

Several classes of chemical reagents are used to aid the concentration process by enabling a selective flotation of certain minerals. These reagents depend on the nature of the ore, the type of selective flotation required, and vary from organic compounds to cyanide to soda ash to sulphur dioxide. Clarke (7) provides a listing of some reagents, their formula and explicit purpose in the flotation process.

In certain ore milling operations, however, reducing sulphur compounds must be used to enable the selective flotation of certain minerals. These compounds are generally in the form of alkaline sulphides, hydrosulphides, sulphites and sulphur dioxide, their use having developed from a combination of efficiency, practicality and economics. As examples, from Lendrum (17):

(i) Hydrosulphite (NaHS) is used as a copper depressant in the separation of copper minerals from molybdenite by flotation.

(ii) Akaline sulphides and bisulphites are depressors of sphalerite and pyrite in the flotation of copper minerals such as chalcopyrite or lead minerals such as galena.

(iii) The use of sulphur dioxide to depress galena in a copper-lead separation, or the removal of lead, as galena, from a copper concentrate.

For the case of sulphur dioxide, its use results in an increase in polythionate concentrations. This can be explained by (equations 3 and 4), and reactions 4, 5, 8 and 9.

$$SO_2 + H_2O \quad H_2SO_3 \quad H^+ + HSO_3^- \tag{8}$$

$$2H^+ + S^{2-} + HSO_3^- + S_2O_3^{2-} \quad H_2S_3O_6^{2-} + HS^- \tag{9}$$

It is expected that mills which use sulphur dioxide could have polythionate concentrations of more than 1000 mg/l in the wastewater, Uko (29). An alternative to the use of sulphur dioxide is cyanide. However, the environmental effects of this compound are more damaging.

2.2.4 Water Recycling

The rate of dissolution of sulphide ions from ore particles, governed by reaction (1), is proportional to the alkalinity of the milling water, the length of time the ore particles are exposed to high pH in the mills and flotation circuits, the water temperature and the degree of agitation. When the pH, agitation, and water temperatures are held approximately constant, the longer the period of exposure of water to the minerals, the more polythionates can be expected in the water. Each time the water is recycled, it is re-exposed to the ore prolonging the period of exposure in comparison to water that is used only once.

Therefore, the concentration of polythionates in both types of mills which recycle water, those that use reducing sulphur compounds and those that do not, will increase.

2.3 Treatment Practices

The most common form of waste treatment system employed by the base metal mining industry is an impoundment, referred to as a tailings pond, into which mill process effluent and other waste flows (mine acid drainage and contaminated surface drainage) are discharged.

2.3.1 Tailings Ponds

Tailings ponds came into existence between 1957 and 1967, (7), prior to which both contaminated mine water and tailings slurry from mills were disposed of, untreated, into the nearest lake or depression.

Their major functions were for the safe disposal of large volumes of solid wastes generated in the course of milling ores, and to decrease levels of suspended solids in the decant. However, due to increasingly more stringent effluent quality standards and a deteriorating environment around mining areas, tailings ponds were required to provide a large degree of chemical treatment to the liquid wastes. Thus, a typical pond may be required to simultaneously perform some or all of the following functions, according to Bell (4):

(i) removal of tailings solids by sedimentation;
(ii) acid neutralization;
(iii) formation of heavy metal precipitates (as hydroxides);
(iv) sedimentation of heavy metal precipitates;
(v) perpetual retention of settled tailings and precipitates;
(vi) stabilization of oxidizable constituents, e.g., thiosulphate to sulphate;

(vii) balancing action for influent quality and quantity fluctuations; and,

(viii) storm water storage and flow balancing.

The most critical treatment processes performed are sedimentation, oxidation and ultimate solids disposal.

2.3.2 Heavy Metals Removal

Effluent levels of heavy metals from mining and milling processes are high, due to acid production by bacteria and the subsequent leaching of heavy metals. Table 5 lists characteristics of some typical mine waters.

Heavy metal removal is achieved by addition of lime to precipitate heavy metals as hydroxides. Settling of the precipitate takes place in the tailings pond. Table 6 lists theoretically obtainable levels of some metals under optimum pH conditions, and practical obtainable levels from waste treatment.

2.3.3 Thiosalts Removal

Thiosulphate and other partially oxidized sulphur compounds originate from the use of sulphur reducing compounds in the flotation circuit of milling operations. The thiosulphate produced varies in amount, but a value of 1000 mg/l is typical.

According to Bell (4), where thiosulphate concentration exceeds, approximately, 100 mg/l it is necessary to provide a separate treatment operation for thiosulphate oxidation. Thus, 100 mg/l is apparently an

TABLE 5 CHEMICAL CHARACTERISTICS OF MINE WATER FROM SELECTED MINES, AFTER CLARKE (7)

	New Brunswick		Ontario		
Characteristic	Brunswick 12	Heath Steele	No. 1	No. 2	No. 3
Operation	Pb,Zn,Cu	Cu,Pb,Zn,Ag	U	Fe	Cu,Zn,Pb,Ag,Au
pH	5.2	3.3	2.3	2.6	3.9
Turbidity - JTU	---	---	---	70	2070
Suspended Solids (ppm)	---	---	15	355	130
Dissolved solids	---	---	6155	3825	---
Chloride (ppm)	---	---	621	---	11
Sulphate	1389	1066	2800	2280	1136
Copper	0.06	39.0	---	0.96	3.04
Lead	0.4	90.0	---	0	0
Iron (total)	0.5	2.0	280	960	182
Manganese	---	---	---	83	3.68
Zinc	35.0	220	---	0.97	16.4
Cadmium	0.004	0.25	---	0.02	0
Arsenic	---	---	---	0.38	---
Magnesium	70.0	4.0	---	12	---
Potassium	8.0	4.9	---	5.1	---
Sodium	42.5	15.5	---	7	---
Calcium	450	120	---	101	---
Hardness	1411	316	---	---	---

TABLE 6 THEORETICALLY OBTAINABLE LEVELS OF METALS UNDER OPTIMUM pH CONDITIONS, AND PRACTICAL OBTAINABLE LEVELS FROM WASTE TREATMENT, AFTER CLARKE (7).

Metal	Theoretical Concentrations (ppb)		Practical Concentrations (ppb)	
	pH	conc'n	Average	Best
Fe(as Fe^{3+})	8	< 1	1000	300
Pb^{2+}	8	< 1	100	50
Cu^{2+}	9.5	1 - 7	30	20
Zn^{2+}	10.0	10 - 60	150	50
Cd^{2+}			40	10
As			50	

upper limit or the amount of thiosulphate capable of being oxidized in a tailings pond.

Existing practice in Canada for the separate treatment of thiosulphate wastes is with lagoons. According to Scott and Bragg (24) there are only two mining operations in Canada employing full scale thiosalt stabilization processes, both using biological oxidation. The first mine was a lead/zinc milling operation with a mill effluent concentration of 1000 mg/l thiosulphate. A lagoon (although not specified as to aeration or extent of mixing, or if in fact a holding pond) was provided downstream of the tailings pond with a thirty day theoretical detention time. During warm weather, thiosulphate reduction of 80 percent was achieved. However, during winter months the system operated less efficiently with a thiosulphate reduction of less than 20 percent. No data is given on the conversion of thiosulphate to polythionates or sulphates. The second mining operation reported an influent thiosulphate concentration to a ponding system of between 200 and 300 mg/l, and was able to compensate for the influence of temperature by using a retention time of one year. Essentially complete thiosulphate stabilization was reported with effluents characterized by COD values of less than 1 mg/l in comparison with feed strengths of 50 mg/l.

2.4 Ecological Observations and Significance

Any environmental effects of effluent from mill process wastes will depend on the concentrations of toxic compounds contained therein (which are factors of the chemical characteristics of the process water) and, ultimately, will depend on the extent and degree of treatment prior to discharge to the receiving stream.

Characteristics of typical mill process effluents, with respect to unoxidized sulphur compounds, are high thiosulphate and sulphate concentrations and an alkaline pH at the point of discharge. Heavy metals, the concentration of which depend on the removal efficiency during treatment, are important in so far as their toxic effects are concerned. Table 7 is a summary of a typical mill process wastewater from selected Canadian mines.

2.4.1 From Unoxidized Sulphur Compounds

2.4.1.1 Thiosulphate

Thiosulphate and polythionates, collectively termed thiosalts, are the principal unoxidized sulphur compounds contributing to environmental problems. Typical effluent thiosulphate concentrations are in the neighbourhood of 1000 mg/l, although this value varies. Toxicity of the thiosalts may be caused directly by the anion or by their ability to generate acid in solution (see Section 2.4.1.2). Clarke (7) presents some toxicity data for the thiosulphate anion which is summarized in Table 8.

2.4.1.2 pH

On discharge to the receiving stream, the effluent pH is usually alkaline (due mainly to the addition of lime to remove heavy metals) with a range from 7.0 to 9.0, and a maximum of 11.0. Highly

TABLE 7 A SUMMARY OF CHARACTERISTICS* OF PROCESS WATERS FROM SELECTEᴾ CANADIAN MINES, AFTER CLARKE (7)

Operation	Anaconda Cu	New Brunswick Brunswick 12 Pb,Zn,Cu	Heath Steele Cu,Pb,Zn,Ag	North West Territories Giant Au	Echo Bay Ag,Cu	Terro Ag,Cu
pH	9.6	6.4	9.1	>9.4	8.2	7.9
Alkatinity	70.6	35.3	80.9	198	85.9	41.0
Turbidity - JTU	>1000			>1000	> 5000	>7000
Conductance umo/cm	1167			1344	50	206
Chloride				89.8	22.6	12.4
Sulphate	508	3306	669	404	39.9	20.0
Thiosulphate	87.6	888	110			
Copper	7.1	0.05	4.6	17.0	0.002	0.004
Lead	10.0	4.0	20.0	<0.005	< 0.004	<0.004
Iron (total)	368	7.4	0.11	0.31	0.02	
Manganese				0.005	0.19	<0.01
Zinc	12.0	12.0	51.0	2.2	0.002	0.01
Cadmium	0.03	0.003	0.02			
Arsenic	13.0			11.0	1.0	11.0
Magnesium	0	7.0	0.2			
Potassium	6.0	22.0	1.9	25.0	18.0	22.5
Sodium	4.1	595	18	63.8	15.8	9.5
Calcium	280	300	875	146	25.3	12.8
Hardness	699	777	2184	390	108	37.2

* ALL VALUES IN mg/1 EXCEPT pH AND WHERE OTHERWISE INDICATED.

TABLE 8 TOXICITY DATA FOR THIOSULPHATE, as $Na_2S_2O_3$, after Clarke(7)

Chemical	Species	Exposure	Concentration (ppm)	Remarks
Thiosulphate $Na_2S_2O_3$	Daphnia magna	100hr	805	LC50*
"	"	25hr	2,245	
"	"	--	< 520	Threshold for immobilization
"	Polycelis nigra		8,400	ILL**
"	Notropis atherinoids	120hr	5	ILL at 18°C
"	Gambusia affinis	96hr	24,000	LC 50

* Median lethal concentration

** Incipient Lethal Level

alkaline waters, such as found in the immediate vicinity of the discharge area, are toxic to aquatic life.

Several investigators have studied toxic effects of high pH waters both in the laboratory and in the field. The main source of information, for this report, regarding these investigations is from a survey of water quality criteria by the European Inland Fisheries Advisory Commission (EIFAC (10)) and a summary of the more pertinent information on toxicity studies in given below.

Of the laboratory observations,

(i) Brandt found that the minimum lethal pH value for trout was 9.2, slightly lower than the values found for rainbow trout by Jordan and Lloyd, who found that the median lethal pH value for a 15-day exposure was 9.5. Brandt also found that the minimum lethal value for perch was 9.2, roach 10.4, carp 10.8, pike,10.7, and tench 10.8.

(ii) Sprague reported that 5 percent of a batch of 40 yearling Atlantic salmon died within six weeks when kept in a water of pH 9.5.

(iii) Rosseland reported that an alkaline effluent was toxic to young salmon and brown trout, a pH of 9.7 being lethal within a day whereas none died during 1-1/2 days at pH 9.0.

(iv) Krishna found that with eggs and alevins of trout, mortalities occurred above a pH value of 9.0, but the length of exposure is not given.

(v) Volodin found that the various development stages of burbot eggs showed different sensitivities to alkaline waters, the most sensitive stage being that of embryo segmentation when a pH value of 8.0 killed half the eggs. Resistance increased after this stage, but even at pH 9.0, hatching was delayed.

(vi) Sperm of common carp had a lower period of motility when the pH value of the water was raised to 8.2-9.5, and pH values of above 9.0 were found to be lethal.

Field observations are more limited due to various uncontrollable factors (temperature, dissolved oxygen level, hardness, background contamination, etc.) but,

(i) Eichler reports that some rainbow trout in a lake were killed when the pH value rose above 10.2, but that fish in a river tolerated a rise to 9.4.

(ii) In Scandinavia, Dahl records a fish kill in Lake Lyngby (Denmark) where the pH rose to between 10.3 and 10.6, and mortalities occurred in Lake Ranninge (Sweden) when the pH of the water rose to between 8.4 and 9.5

In general, however, although field observations are the more ideal, significance placed on the toxic effect of high pH values may be questioned due to several other natural factors operating simultaneously either to enhance or detract from the effect of pH. Specifically, dissolved oxygen and carbon dioxide concentrations affect the lethal levels of pH, (10).

Additional significance of high pH values are the induced toxic effects of other compounds. Examples are the nickelocyanide complex which is 500 times more toxic at pH 7.0 than at 8.0, ammonia, (originating from ammonia nitrate, used for blasting purposes in the mines) which is about one tenth as toxic at pH 7.0 than at 8.0, and zinc . Although zinc in solution may be precipitated as the basic carbonate at alkaline pH values, the precipitate can be highly toxic to fish if kept in suspension (7).

The mode of toxic action of hydroxyl-ions is to destroy the gill and skin epithelium (tissue forming outer layer of mucous membrane). Furthermore, in EIFAC (10), Eichler reports that trout found dying at a pH value of 10.2 had frayed dorsal and claudal fins and were blind. Fish hunt by sight. A similar condition was reported for carp at a pH value of above 9.0.

According to Duodoroff and Katz (9), fish may be more tolerant of alkaline than acidic conditions, the explanation being that carbon dioxide given off at the gill surface may have some effect in reducing the pH in the immediate neighbourhood of the gill filaments, thus providing some degree of protection.

In summary it appears that chronic exposure to pH values above 10.0 are harmful to all species studied, while salmonid and some other species are harmed at pH values above 9.0.

The oxidation of thiosulphate and the polythionates proceeds in the receiving stream due to the action of Thiobacill· species, usually _T. thiooxidans_ (the predominant species) and _T. ferrooxidans_. From the practical viewpoint the complexities of the biological processes may be expressed in terms of three main chemical transformations, after Graham (11).

Complete oxidation of thiosulphate to sulphate:

$$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (10)$$

Partial oxidation of thiosulphate to thionates:

$$nS_2O_3^{2-} + (n-2)H_2O + 2(5-n)O \rightarrow 2S_nO_6^{2-} + 2(n-S)OH^- \qquad (11)$$

where "n" may take the value 2-6 and, oxidation of thionates to sulphate:

$$SnO_6^{2-} + (n-1)H_2O + (3n-5)O \rightarrow nSO_4^{2-} + 2(n-1)H^+ \qquad (13)$$

This net generation of acid in the receiving stream with depression of pH to the range 2.5-3.5, as reported by Schmidt and Conn (22), causes additional ecological problems as the hydrogen ion, both directly and indirectly, is toxic to many forms of aquatic life.

EIFAC (10) reported on investigations dealing with the effects of low pH values on various species of fish. A summary of the more pertinent information on toxicity studies taken from EIFAC follows. Of the laboratory observations,

(i) Dahl found that 80 percent of trout in the yolk sac stage died within 20 days at pH values 4.7-5.4, and 10 percent died in the range 5.1-5.7.

(ii) Grande reported that salmon in the yolk sac stage were found to have a median lethal pH value of 4.5 at 12 days; also, yearling brown trout taken from a soft acid river (pH 5.85) died within 12 to 14 hours at a pH value of 3.3 and survived a pH value of 4.1 for 7 days. Grande also reported that the hatching success of salmon eggs in a water acidified with sulphuric acid to give a pH value of 4.59 was 96 percent compared with only 48 percent at a pH value of 4.34; moreover, only 50 percent of eyed brown trout ova hatched in a solution of pH 4.77.

(iii) Lloyd and Jordan found that roach and rainbow trout had the same 8-day median lethal pH value of 4.2, although roach had shorter survival times at pH values between 3.0 and 4.1.

(iv) Volodin showed that the resistance of the various developmental stages of burbot embryos to acid waters varied and successful development could only take place within a narrow pH range. The most sensitive stage was that of embryo segmentation at which a pH value of 6.0 was the critical lower level but during subsequent development the critical level lowered to 5.0.

(v) Dyk and Lucky found that the period of motility of carp sperm was reduced in water acidified with peat to a pH value of 6.5, and Elster and Mann demonstrated a decreased motility of carp sperm at pH 4.5 and lower pH values were lethal to them.

Of the field observations,

(i) Natural populations of brown trout have been found in waters of pH value as low as 4.5, and Eastern brook trout found in waters with a pH value of 4.1. However, salmonids have been reported absent in waters when the pH value fell below the range 4.6-4.8.

(ii) Roach, perch, pike and bream have been found in a Swedish lake where the pH range is from 3.7-3.8, and an iron content of 0.3-1.2 ppm Fe. Apparently, roach can survive at lower pH values than those found to be lethal in laboratory experiments.

(iii) Rhyanen reports a Finnish lake, into which an acid stream discharges, with a large area where tho pH varied from 4.2-4.4. Bream, roach, perch and pike were present in this area, but only pike were able to breed.

The mode of toxic action of hydrogen ions, according to EIFAC (10) has been ascribed to the precipitation of mucus on the gill epithelium causing death by suffocation, or by precipitation of protein within epithelium cells. This cause of death has been termed "coagulation film anoxia" and Jones (13) enlarges on the description of EIFAC by stating Ellis' rendition of the toxic process as threefold in its attack on the respiratory apparatus. First, the spaces between the gill filaments become filled with precipitate, so that the water flowing through the bronchial chambers cannot reach the gill filament cells; secondly, the spaces between the gill lamellae become filled, so that movement of the gill filaments become impossible, and this condition affects the circulation of blood in the gill capillaries; thirdly, this stasis affecting the blood circulation in the gills, leads to heart block, the heart action dropping to about half the normal rate.

EIFAC (10) report Lloyd and Jordan as finding no evidence of gill tissue damage or precipitated mucus in rainbow trout taken at death after a 7-1/2 hr exposure to a solution of pH 3.4, and Douderoff and Katz (9) feel that the importance of coagulation of mucus and cell proteins of the gill membranes and resulting interference with respiratory exchanges as a cause of death in acid waters as being overemphasized. However, Jones (13) shows more researchers as favouring the "coagulation film anoxia" theory as the mechanism of death.

Other mechanisms involved in the death of fish are acidaemia (a lowering of the venous blood pH) and development of a hypersensitivity to bacteria below a pH of 5.5. Also, the life cycles of some fish parasites are affected by pH value.

Table 9 is a summary of the effect of pH values on fish.

Low pH values also affect the lives of inverterbrates, source of food for fish. In a study on the effect of low pH on the survival and emergence of various aquatic insects, of value as fish food, Bell (5) found that of nine species of aquatic insects tested the most tolerant species was the caddisfly Brachycentrus americanus, a widespread and important fish food, with a 30-day TL_{50} of pH 2.45, and the least tolerant the mayfly Ephemerella subvaria with a 30-day TL_{50} of pH 5.38. On the emergence of these species at low pH, six of the nine were between pH 5.0 and 5.9, with B. americanus again the most tolerant with emergence at pH 4.0.

In general, the aquatic species tested differed markedly in their tolerance to low pH values, with caddisflies very tolerant to low

TABLE 9 SUMMARY OF THE EFFECT OF pH VALUES ON FISH, AFTER EIFAC (10)

RANGE	EFFECT
3-0-3-5	Unlikely that any fish can survive for more than a few hours in this range although some plants and inverletrates can be found at pH values lower than this.
3-5-4-0	This range is lethal to salmonids. There is evidence that roach, tench, perch and pike can survive in this range, presumably after a period of acclimation to slightly higher, non-lethal levels, but the lower end of this range may still be lethal for roach.
4-0-4-5	Likely to be harmful to salmonids, tench, bream, roach, goldfish and common carp which have not previously been acclimated to low pH values, although the resistance to this pH range increases with the size and age of the fish. Fish can become acclimated to these levels, but of perch, bream, roach and pike, only the last named may be able to breed.
4-5-5-0	Likely to be harmful to the eggs and fry of salmonids and, in the long term, persistence of these values will be detrimental to such fisheries. Can be harmful to common carp.
5-0-6-0	Unlikely to be harmful to any species unless either the concentration of free carbon dioxide is greater than 20 ppm, or the water contains iron salts which are precipiated as ferric hydroxide, the toxicity of which is not known.
6-0-6.5	Unlikely to be harmful to fish unless free carbon dioxide is present in excess of 100 ppm.
6.5.9.0	Harmless to fish, although the toxicity of other poisons may be affected by changes within this range.
9.0.9.5	Likely to be harmful to salmonids and perch if present for a considerable length of time.
9-5-10-0	Lethal to salmonids over a prolonged period of time, but can be withstood for short periods. May be harmful to development stages of some species.

Continued on next page.

10-0-10-5	Can be withstood by roach and salmonids for short periods but lethal over a prolonged period.
10-5-11-0	Rapidly lethal to salmonids. Prolonged exposure to the upper limit of this range is lethal to carp, tench, goldfish and pike.
11-0-11-5	Rapidly lethal to all species of fish.

Reference is made to different species on the basis of information known to us; the absence of a reference indicates only that insufficient data exist.

pH, stoneflies moderately tolerant and mayflies fairly sensitive. With few exceptions, however, the aquatic insects are more tolerant pf acidic conditions than fish. From the practical point of view, this means that insects could survive conditions which would prove detrimental to fish, and thus, would serve as a food resource when fish repopulation occurs.

Although microorganisms are not immune from the effects of acid waters they can survive, and Dugan, et al.(8) report the work of Lackey, who examined several streams, each having a pH below 4.0, and observed 11 genera of flagellates, 7 rhizopods, 12 ciliates, the algae Ulothrix zonata and Euglena mutabilis and bacterial masses in the form of colourless or light brown gelatinous "streamers". Joshep is also reported by Dugan, et al. as isolating, from acid streams (pH 2.0-4.0) in Ohio, bacteria of the genera Bacillus, Micrococcus, Sarcina, Escherichia, Aerobacter, Thiobacillus, Crenothrix and Microsporium.

In a study on aerobic heterotrophic bacteria indigenous to pH 2.8, Dugan, et al.(8) determined that the acid "streamers" found in low pH waters consist of various species of bacteria trapped within "an extracellular fibrillar polymer network". Inorganic salts, amply present in mine waters, appear to be precipitated within the polymer network, the possible result of a pH differential within the microenvironment of the slime matrix and the acid water. Thus, the acid environment is not as hostile to microorganisms as it is to fish, and this survival mechanism of bacteria could account for the survival, but not elimination of E. coli and A. aerogenes from acid drainage, according to Dugan, et al. (8).

Additional environmental significance of low pH values are the induced toxic effects of other compounds, and the examples cited for high pH values also apply here. One other induced toxic effect, restricted to low pH values, is due to the release of free carbon dioxide when acid is generated in (or where acidic wastes are added to) bicarbonate rich waters. The reactions is

$$\text{acid} + \text{bicarbonate} \rightarrow \text{salt(carbonate)} + \text{water} + CO_2\uparrow,$$

and if the water is hard, (i.e. high alkalinity), sufficient free CO_2 may be liberated to be toxic to fish, even though the pH value does not fall to a level normally considered to be lethal.

EIFAC (10) report Lloyd and Jordan as showing that in water containing 10 ppm free CO_2 or less, the median lethal pH value for fingerling rainbow trout was 4.5 after 15 days; exposure, but with water containing more than 20 ppm free CO_2, the median lethal pH value rose to 5.7. (Although fingerling trout were used, EIFAC, also report no correlation between size of fish and sensitivity). In fact, many laboratory investigations on the effects of low pH have been rendered invalid or difficult to interpret due to failure to determine the CO_2 content during the investigation.

Carbon dioxide, when present in concentrations of 2-3 percent, acts as a respiratory stimulant in man, and according to Jones (13), due to vague and contradictory evidence, it is uncertain as to whether the gas acts similiarly in fish. However, Jones reports Rogers as noting an increased carbon dioxide tension causing an increased depth of respiratory movement in goldfish; similar observations have been noted for minnow and perch.

Selected information from Jones (13), on laboratory investigations on CO_2 toxicity, shows the importance of dissolved oxygen in allowing fish to cope with carbon dioxide.

(i) Wells showed that provided that the oxygen supply is ample, fish can survive moderately high concentrations of CO_2; the most sensitive species surviving for 34 hours, a CO_2 concentration of 35-50 cm^3/l at an oxygen concentration of 8-10 cm^3/l.

(ii) Black et al show that carbon dioxide has an important effect on fish respiration in that the concentration in which is is present determines the extent to what the available oxygen can be utilized. Their results showed that as the carbon dioxide concentration was increased, the residual oxygen in the water also increased, indicating that less oxygen had been used.

(iii) The importance of oxygen is again indicated by Alabaster et al (13) who show that oxygen thresholds for rainbow trout are dependent on the carbon dioxide tension. At 16.5°C, with the CO_2 tension zero, the fish survived over 24 hours with the oxygen at 15 percent saturation; at 30 ppm CO_2, the water had to be 25 percent saturated to permit the same survival time; at 60 ppm CO_2, 30-40 percent. At 120 ppm CO_2, the fish died in 8 hours in water saturated with oxygen, and at 240 ppm CO_2, the fish lived for 1 hour.

Douderoff and Katz (9) present information on concentrations of CO_2 toxic to various species of fish and concluded that althoug some species of fish are very resistant to CO_2, concentrations between 100 and 200 ppm are rapidly lethal to most fish, and that concentrations of

CO_2 as low as 50 ppm may be lethal to some fish on prolonged exposure, or if there is a low oxygen level.

The mode of toxic action of carbon dioxide is that at high concentrations (150-600 ppm) it produces an anaesthetic effect, with resulting stupefication and insensibility, and a gradual loss of consciousness due to the inability to use oxygen. Thus, death is presumably by asphyxiation, according to Douderoff and Katz (9). Also, CO_2 has the ability to penetrate readily into living tissue where its effects may be related to its acidic nature.

2.4.1.3 Sulphate

Sulphate in the receiving streams has two sources of origin. The first is from the oxidation of sulphide minerals, and the second is from the biological oxidation of thiosulphate and polythionates contained in the mill process effluent.

As the final oxidation state for sulphur compounds, sulphates are often the largest single constituent of mining effluents with concentrations varying from 280 ppm to 7000 ppm. Table 7 shows representative sulphate concentrations from some Canadian mines.

Toxicity of sulphate compounds, according to Jones (13) depends on the associated cation, with copper and zinc sulphates being highly toxic due to the Cu^{2+} and Zn^{2+} cations. (Solutions of as low as 1 ppm copper and 0.5 ppm zinc are toxic to brown trout and rainbow trout, respectively, from Jones). However, at concentrations normally found in mine effluents, sulphates may have harmful effects on freshwater ecosystems.

Table 10 presents results on the toxicity of sodium and magnesium sulphate. It should be noted that the toxicity may be the result of the Na^+ or Mg^{2+} ions, the SO_4^{2-} ions or both. However, as sodium and magnesium are among the least toxic metals, the interpretation is clarified somewhat.

2.5 Literature Review on the Biological Oxidation of Thiosulphate

Although the awareness of unoxidized sulphur compounds from mill process wastes contributing to increases of acidity in rivers is recent (23), probably the first study conducted into the problem was in 1913 by Lockett (18), whose bench scale bacterial filter was the first biological reactor used for the study of thiosulphate oxidation.

The bacterial filters consisted of stonewater pipes, 24 in (60 cm) in length by 4 in (10 cm) in diameter filled with 1/4 in (0.6 cm) to 1 in (2.5 cm) clinkers (a type of hard brick) over which sodium thiosulphate ($Na_2S_2O_3$) in various concentrations up to 5 g/1, were passed. A once through contact time between the filter and thiosulphate solution of 2 hours was used. Depending on the initial strength of thiosulphate, the number of contacts varied from 4 to 6. For instance, a solution containing 910 mg/1 was completely oxidized in 5 contacts.

Regardless of the initial thiosulphate concentration, however, the end product (filtrate) contained large quantities of sulphate and was "generally acid to methyl orange". A conversion of thiosulphate to sulphate greater than 70 percent was obtained.

Qualitative examination of the filtrate while the contact

TABLE 10 SOME TOXICITY DATA FOR SODIUM AND MAGNESIUM SULPHATES, AFTER CLARKE (7)

	Cation	Exposure	Concentration (ppm)	Remarks
Amphipods	Na^+	96 hr	990	LC50
Culex larvae	"	48 hr	13,350	LC50
Daphnia Magna	"	96 hr	630	LC50
" " adult	"	96 hr	4,547	LC50
" "	"	100 hr	4,547	Lethal
" "	"	Not stated	5,000	Not harmful
Lymnaea species eggs	"	96 hr	3,553	LC50
Shiners	"	120 hr	100	Lethal
Lepomis macrochirus	"	96 hr	12,750	LC50
Gambusia affinis	"	96 hr	16,500	LC50
Perca flavescens	"	24 days	7,500	Not harmful
Cyprinus carpio	"	24 days	15,000	Not harmful
Gambusia affinis	Mg^{2+}	96 hr	15,500	LC50 in turbid water
Perca flavescens	"	14 days	20,900-28,400	Lethal in cistern water
" "	"	78 days	24,500-27,500	Lethal in well water
Anguilla rostrata	"	> 25 hr	12,000	Maximum tderated concentration

was in progress, showed that trithionate was almost invariably absent, and when present, was in trace amounts; that tetrathionate appeared to be the main intermediate product, sometimes occurring alone, but frequently with small quantities of pentathionate; and, that pentathionate led a transient existence being oxidized to sulphate before the complete oxidation of the solution. Additional experimentation on the ability of the filter to oxidize the intermediate thionates revealed that dithionate is not oxidized to any extent but the tri-, tetra- and pentathionates in concentrations up to 1 g/l, were oxidized to sulphates with production of free acid.

It was concluded that the oxidation of thiosulphate was most probably due to bacterial action, although no attempt was made to isolate and describe the bacteria beyond the fact that they were "very small cocci" and they could not be cultivated on gelatine, and was possibly assisted by the physical and chemical properties of the filtering materials.

Substantiation of the bacterial action mechanism as being responsible for thiosulphate oxidation was given by Heukelekian and Lassen (12) in a study on the oxidation of reduced sulphure compounds in domestic sewage. They used sodium sulfite (Na_2SO_3), sodium sulfide (Na_2S), sodium bisulfite ($NaHSO_3$), and sodium thiosulfate ($Na_2S_2O_3$) as the reduced sulfur compounds. These substances in concentrations of 100 mg/l as S were added to sewage, heat sterilized sewage, a mixture of activated sludge and sewage, and a mixture of trickling filter slime and sewage. All substances except $Na_2S_2O_3$ were oxidized as rapidly in sterile sewage or in non-sterile sewage when oxygenated.

In the absence of microorganisms, $Na_2S_2O_3$ was not oxidized. In addition, best results for thiosulphate oxidation were obtained with the sewage and trickling filter slime mixture, although the difference between that and the activated sludge-sewage mixture was marginal.

Further work by Heukelekian and Aulenbach (2) on thiosulphate oxidation showed that activated sludge could be acclimatized to remove thiosulphate. In a 6 ℓ batch reactor activated sludge was capable of removing up to 750 mg/l of thiosulphate as sulphur with a 6 hour aeration period, of which up to 250 mg/l was oxidized completely to sulphate. Intermediate compounds in the oxidation process, such as tetrathionate, were acknowledged but not tested for, although elemental sulphur was thought to cause whitening of the sludge. One problem, however, with the sludge fed thiosulphate was that the sludge volume index (SVI) was higher than that of a control receiving no thiosulphate.

Although the mechanism in the oxidation was assumed to be biological, no attempt was made to isolate and describe the bacteria involved, nor were values of the activated sludge pH during oxidation stated.

Sources of thiosulphate are not completely restricted to mill process wastes or domestic sewage, and in a comprehensive series of experiments on the treatment of coking wastewaters Graham (11) used mixed cultures of thiosulphate oxidizing bacteria Thiobacillus thiocyanoxidans and Thiobacillus thioparus to successfully oxidize both synthetically prepared ammonium thiosulphate solutions (containg some thiocyanate) and effluent (containing thiosulphate) from catalytic oil gas plants.

A complete mix (suspended growth) reactor without solids recycle, with a capacity of 3.6 ℓ maintained at a temperature of 25°C ± 2°, supplied with diffused aeration and provided with an automatic pH control which maintained the pH between 6.0 and 7.5 with sodium carbonate to neutralize the sulphuric acid formed, was used for both types of influent. Hydraulic retention times of 1/2, 1, 2 days and values in between were obtained by varying the influent flowrate.

The synthetic feed solution contained thiosulphate in concentrations from 3.0 to 10.0 g/l, and complete removal of thiosulphate was obtained at loadings of up to 347 lb S_2O_3/1000 ft^3-day (5.83 kg/1000 m^3-day) with retention times at 1.2 days and an average pH varying from 5.7 to 6.1. At a loading of 566 lb S_2O_3/1000 ft^3-day (9.51 kg/1000 m^3-day) with a retention time of 1.1 days and an average pH 6.8, 91.7 percent treatment efficiency was attained.

For the study using diluted and undiluted catalytic oil gas plant wastes, at thiosulphate loadings from 53 to 436 lbs S_2O_3/1000 ft^3-day (0.89-7.32 kg/1000 m^3-day), 99.7 to 100 percent of thiosulphate was oxidized. Retention times for the individual runs in this study varied from 0.5 to 1.7 days with the average pH varying from 3.5 to 7.1, indicating a treatment efficiency under unfavourable conditions.

In all experiments, a noticeable feature of the process was the absence of separable solids. This fact has subsequently been noted by later experiments (22,3) when either pure or mixed cultures of thiosulphate oxidizing bacteria were used.

Additional information from Graham's work indicated that batch studies in 2 ℓ reactors achieved thiosulphate oxidation rates of 2100 lb S_2O_3/1000 ft^3-day (35.28 kg/1000 m^3-day) when an active culture of microorganisms is used and that periods of up to a month without feed are not permanently detrimental to the culture provided that aeration is maintained.

Schmidt (22) continued research into thiosulphate oxidation with various studies on the cultivation of thiobacilli (to obtain a species appropriate for thiosulphate oxidation), limited batch type experiments (using results from the culturing study), and the application of results from both studies to several continuous flow reactors without recycle.

From the cultivation study and batch type experiments, it was learned that Thiobacillus novellus and Thiobacillus ferrooxidans were incapable of growth in a thiosulphate medium, and that Thiobacillus thiooxidans, after a lag period of five days was capable of oxidizing thiosulphate in concentrations of up to 200 mg/l. Best results, however, were obtained with Thiobacillus thioparus when complete removal of 7000 mg/l of thiosulphate was obtained overnight. Additional work with T. thioparus suggested a first order reaction rate with respect to thiosulphate oxidation.

The bioreactors (continuous flow) were started from batch reactors using 1000 ml of tailings pond effluent as substrate (thiosulphate concentration 750 mg/l), supplemented with nitrogen and phosphorous, and as innoculum 500 ml of effluent receiving stream water, supplying T. thiooxidans. After eight days, when thiosulphate utilization occurred, continuous flow without recycle was started with an influent flowrate 1.68 l/day, retention time 2 days, influent thiosulphate concentration 1000 mg/l at pH 4.0, and the mixed liquor at pH 2.0.

Results from the continuous flow studies with regard to retention time indicated that a retention time of 18 hours at room temperature was sufficient for complete removal of thiosulphate, whereas a retention time of 6 hours was capable of about 90 percent thiosulphate oxidation. Under cold temperature conditions, at 2°C, a retention time of 41 hours was sufficient to oxidize 600 mg/l of thiosulphate. With feed thiosulphate concentration raised to 1000 mg/l, at 2°C, reactor failure occurred. Studies with T. thioparus under the same conditions of influent characteristics and room temperature showed that a retention time of 24 hours effectively removed 1000 mg/l of thiosulphate.

Operational problems encountered during these studies were a lack of significant biomass concentration for the volatile suspended solids (VSS) test, and poor setting unmodified by chemical coagulants of the biomass under quiescent conditions, precluded gravity recycle. Both these problems have subsequently been reported (3,11,14), for suspended growth systems employing either pure or mixed cultures of thiobacilli for thiosulphate oxidation.

With the initial premise that some industrial effluents contain significant concentrations of thiosulphate, Kreye, et al. (14)

experimented with a biological system capable of concurrently removing both thiosulphate (from industrial wastes) and organic matter (from domestic sewage) in one unit.

Using combinations of high strength thiosulphate industrial wastes and primary sewage as the influent and activated sludge as the seed in 10 ℓ bench scale units, the system responded well with 95 percent thiosulphate removal from an influent containing 750 mg/l of thiosulphate, and reduction in pH from 8.3 to 2.7.

Further increases in the influent thiosulphate concentration had no significant effect on thiosulphate oxidation. With initial thiosulphate concentration at 240 mg/1, MLVSS at 1190 mg/1 and influent pH 7.0, percentage removals for thiosulphate and COD were 95 and about 55, respectively. Effluent pH was less than 4.0. Subsequent reduction of influent thiosulphate to 1000 mg/1 resulted in percentage removals of thiosulphate and COD of 97 and 55, respectively, with MLVSS at 570 mg/1 and effluent pH less than 4.0.

Changing the influent characteristics by the addition of tapwater and nutrients to the same industrial high strength thiosulphate waste, but reducing the amount of primary sewage, resulted in no significant change in the rate of thiosulphate oxidation. However, there was an increase in the percentage removal of COD. With a thiosulphate concentration of 1070 mg/1, MLVSS of 230 mg/1, percentage removals of thiosulphate and COD were 95 and 87, respectively, and the effluent pH was 2.0. At an influent thiosulphate concentration of 2100 mg/1, percent removals for thiosulphate and COD were 95 and 75, respectively, with MLVSS at 240 mg/1 and effluent pH 1.8. At an influent thiosulphate concentration of 3840 mg/l percent removals for thiosulphate and COD were 99 and 87, respectively, with MLVSS at 800 mg/l and effluent pH 1.6.

During these studies, nutritional requirements for nitrogen and phosphorous were low with the amounts supplied, 5.2 mg/l phosphate as phosphorous and 13.5 mg/l nitrogen, being sufficient.

In a further study of thiosulphate oxidation, Kreye, et al. (15) with similar waste and reactor conditions as in a previous study (14) evaluate operational problems for the biological oxidation of thiosulphate.

With a waste consisting of thiosulphate, tap water, nutrients and secondary sewage treatment plant effluent, and activated sludge acclimatized to thiosulphate for over six months, experiments were conducted in 10 ℓ bench scale reactors.

For Experiment 1 with a retention time of 22.8 hours, influent thiosulphate concentration was varied from 1463 mg/l to 4000 mg/l, while the reactor MLVSS varied from a minimum of 100 mg/l to a maximum of 216 mg/l, and mixed liquor pH fluctuated between pH 4.0 and pH 7.0. During this study, there was a 75 percent conversion of thiosulphate to tetrathionate while percent conversion of thiosulphate to sulphate varied from 16 to 6. This poor conversion to sulphate was attributed to low nitrogen and phosphorous concentrations in the influent (5.5 mg/l phosphate as P, and 13.5 mg/l nitrogen). A second experiment was started to determine whether the extent of thiosulphate oxidation could be improved.

For Experiment 2 the phosphate and nitrogen concentrations were raised to 14 mg/l and 33 mg/l, respectively, and the retention time increased to 32 hours. Other influent characteristics remained unchanged. Influent thiosulphate concentration varied from 1532 mg/l to a maximum of 4230 mg/l while the MLVSS varied from a minimum of 131 mg/l to a maximum of 224 mg/l. Mixed liquor pH was consistently lower than in Experiment 1 and was at times below pH 2.0, but depended on whether the reactor was operating efficiently. During this study, conversion of thiosulphate to tetrathionate was much lower than in Experiment 1 and the conversion of thiosulphate to sulphate averaged 78 percent.

The main operational problem encountered during both experiments was poor sludge settling.

In conjunction with, and as a consequence of, the work of earlier studies (11,14,22), BC Research (3) assessed the practicality of using Thiobacillus species to oxidize thiosulphate from flotation-mill wastewaters, and evaluated the efficiency of various biological treatment systems for thiosulphate oxidation.

Assessment of the practicality of Thiobacillus species to oxidize thiosulphate was performed in batch reactors (250 ml Erlenmeyer flasks, 100 ml thiosulphate solution and 5 ml culture) using as thiosulphate oxidizers a culture which contained Thiobacillus thiooxidans, the predominant species, and T. ferrooxidans, isolated from the tailings water, and as feed a synthetic thiosulphate solution. Results from these batch studies show that thiosulphate oxidation rates were the same when the initial pH was 3, 4 or 5, and that the final pH after oxidation was in the range 1.7 to 1.9 regardless of the initial pH. At an initial pH of 6, and above, thiosulphate oxidation occurred, but only after a lag period of about 50 hours.

A decrease in incubation temperature resulted in a decrease in the rates of oxidation. The estimated rate at 2°C was 12 mg/l/hr, which was approximately 1/10 the rate at 23°C and 1/20 the rate at 30°C. The generation times of the culture, of importance when considering residence times, were calculated to be 7-1/2 hours at 30°C, 9.4 hours at 23°C and 8.3 hours at 5°C, showing the significance of longer retention times during cold weather operations. Table 11 lists the oxidation rates of the mixed culture at various monitoring pH and temperature values.

Nutritional requirements of the culture during the batch studies were evaluated by varying the amounts of ammonium and phosphate ions, the most significant of the required nutrients for the Thiobacillus species. Results showed that there was no difference in oxidation rates between a nutritionally complete medium (8.7 mg/l NH_4^+, 2094 mg/l PO_4^{3-}, 0.5 g/l $MgSO_4.7H_2O$, 0.25 g/l $CaCl_2$) and a deficient one containing only NH_4^+ and PO_4^{3-} in the same concentrations as above. With only NH_4^+ present, the rate of thiosulphate oxidation was slower, however complete oxidation still occurred. With 82 mg/l NH_4^+ as the sole nutrient, the oxidation rate was about 40% of the control rate, and with 82 mg/l NH_4^+ and 21 mg/l PO_4^{3-}, the oxidation rate was 50% of that when NH_4^+ was used alone. Thus, these results indicate that, when considering batch reactors, high levels of ammonium and phosphate ions are necessary to maximize the oxidation of thiosulphate.

TABLE 11 BIOLOGICAL OXIDATION OF THIOSULPHATE IN BATCH REACTORS USING MIXED CULTURES ,after BC Research (3).

TEMPERATURE ($^\circ$C)	Thiosulphate ($S_2O_3^{2-}$) Oxidation Rate (mg/l/hr) Initial pH				GENERATION TIME (Hours)
	pH3	pH4	pH5	pH6	
30	240	240	240	4	7.6
23	110	110	105	4	9.4
10	33	33	33	3	22.4
5	16	16	24	1	83.0

With a pure culture of Thiobacillus thioparus to oxidize thiosulphate at various initial pH values and a temperature of 30°C, it was found that the oxidation rate at an initial pH of 3, 4 and 5 was 138 mg/l/hr, and at initial pH 3, after an 80 hour lag, the same rate was obtained. At initial pH 6, the rate decreased to 45 mg/l/hr. This result is surprising, when considering that T. thioparus is not acidophilic, preferring near neutral pH conditions, and as such is in disagreement with Graham (11). At 5°C, oxidation rates with T. thioparus at initial pH values of 3, 4 and 5 were 2.5 mg/l/hr lower than the rate obtained with the mixed culture. See Table

The first of two biological systems studied was an activated sludge unit performed in a Busch Fermenter, which consists of concentrically mounted 2- and 6-litre pyrex cones with air spurged through the bottom. Operational volume was 5.5 ℓ.

With the mixed culture as seed and a synthetic thiosulphate influent, the maximum oxidation rate observed at room temperature was 60 mg/l/hr. It was also noted that bacterial growth occurred over all the surfaces of the fermenter, and did not form a conventional activated sludge floc, paralleling the observations of others (11,14,22). Attempts at creating an artificial sludge floc did not result in an increase in the average oxidation rate which remained at 60 mg/l/hr.

The second biological system studied with respect to thiosulphate oxidation was the Rotating Biological Contactor (RBC) or "Biodisc"*, which utilizes a fixed film of microorganisms to accomplish biological oxidation, and has as a microbiological basis the fact that Thiobacillus species (especially T. thiooxidans) prefer a solid surface upon which to grow.

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*"Biodisc" is a Registered Trade Name.

Units used in these studies had a 6.4 ℓ capacity, with the holding trough divided into three compartments, each compartment containing 33 plexiglass discs. The discs were 8 inches in diameter and 1/2 inch thick with a working surface area of 98.1 square inches (0.681 sq.ft.) and were mounted on a shaft capable of rotational speeds of 1-5 revolutions per minute (rpm).

The studies at room temperature (20°C-22°C) used a synthetic influent with initial thiosulphate concentration 3.6 g/l at pH 4.5. With a flow rate 1.25 l/hr, and residence time 307 minutes, a thiosulphate oxidation rate, over the first 33 discs, of 160 mg/ft^2/hr was obtained. Increasing the flowrate to 2.94 l/hr, residence time 131 minutes, the rate of thiosulphate oxidation, over the first 33 discs increased to 267 mg/ft^2/hr. In both cases, the effluent was at a pH of 1.7 to 1.9.

Decreasing the influent thiosulphate concentration to 1000 mg/l, a level more representative of the mine water that would, realistically, be treated, and increasing the flowrate to 6.4 l/hr, residence time 60 minutes, oxidation rates, over the first 33 discs, of between 220 and 240 mg/ft^2/hr. Increasing the flow to 10.2 l/hr, residence time 38 minutes, resulted in an oxidation rate, over the first 33 discs, of 270 mg/ft^2/hr.

Increasing the influent pH to 9.0, to simulate that of mine water, and maintaining thiosulphate at 1 g/l, with flowrate of 11.4 l/hr and residence time at 34 mins., resulted in an oxidation rate of 279 mg/ft^2/hr, with about 12 mg/l thiosulphate appearing in the effluent.

During these studies, the concentration of NH_4^+ and PO_4^{3-} were 180 mg/l and 461 mg/l, respectively, but later reduction to 18 mg/l NH_4^+ and 64 mg/l PO_4^{3-} had no recorded detrimental affect. The rotational speed throughout was 3.8 rpm.

The studies at lower temperature, 10.5°C and 8.5°C, used an influent containing 1 g/l thiosulphate, 18 mg/l NH_4^+, and 46 mg/l PO_4^{3-}, at a pH of 4.5.

At 10.5°C (±0.5°C), with the flowrate at 7.8 l/hr and shaft rotation at 3.8 rpm, an oxidation rate of 155 mg/ft^2/hr was obtained. Reducing the temperature to 8.5°C (±0.5°C) and simultaneously increasing the flowrate to 10.68 l/hr, with rotation at 3.8 rpm, an oxidation rate of 146 mg/ft^2/hr was obtained, close to the maximum oxidative capacity for the operational conditions as the effluent thiosulphate concentration averaged 190 mg/l. The effluent pH was 2.1 - 2.2.

Retaining the same influent characteristics and with a flow of 10.68 l/day, but reducing the rotational speed from 3.8 to 1.3 rpm resulted in an oxidation rate of 165 mg/ft^2/hr, an increase in the rate obtained at 3.8 rpm.

Reducing the nutrient level of the feed to 8 mg/l NH_4^+ and 5 mg/l PO_4^{3-}, with 1 g/l thiosulphate in the influent and rotational speed at 5 rpm, an oxidation rate of 146 mg/ft^2/hr was obtained, indicating no effect due to reducing the nutrient levels. A further reduction to 4 mg/l NH_4^+ and 5 mg/l PO_4^{3-}, with influent thiosulphate concentration and rotational speed held constant at the previous level, resulted in an average oxidation rate of 128 mg/ft^2/hr. Reducing the speed of rotation, at this low nutrient level, from 5 to 3.3 rpm resulted in an oxidation rate of 122 $mg/ft^2/hr$, showing no significant difference from the rate at 5 rpm.

An analysis of the RBC's ability to operate on tailings pond effluent as feed, was made using a supply of tailings pond water (from a New Brunswick mine), which contained a thiosulphate concentration of 900 mg/l and NH_4^+ and PO_4^{3-} in concentrations of 3.60 mg/l and 0.86 mg/l respectively. The tailings pond water was not supplemented with nutrients.

Results, at first, were unsatisfactory with a maximum oxidation rate of only 88 $mg/ft^2/hr$, occurring over the last third of the RBC, and an effluent thiosulphate concentration of 580 mg/l. However, with acclimatization, the same flowrate and influent thiosulphate concentration resulted in an oxidation rate of 103 $mg/ft^2/hr$, and an effluent thiosulphate concentration varying from 20 mg/l to 220 mg/l. This rather high effluent thiosulphate concentration may be due to low values of NH_4^+ and PO_4^{3-} present in the tailings pond water, and to improve oxidation rates nutrient addition may be necessary.

CHAPTER 3

THEORETICAL CONSIDERATIONS

As stated at the end of Chapter 1, the purposes of this study were to investigate, separately, the effects of influent phosphorous concentrations and retention time on thiosulphate oxidation.

Prior to the start of both studies, activated sludge was gradually acclimatized to increasing concentrations of thiosulphate with periodic additions of Thiobacillus thiooxidans, a member of the genus Thiobacillus.

The genus Thiobacillus, comprises a number of closely related species. The members of this genus are small (measuring 0.5 by 1-3μ), gram-negative, generally motile, polarly flagellated (with the exception of the non-motile Thiobacillus novellus), rod-shaped bacteria, which inhabit a wide variety of marine, freshwater and terrestial environments.

All thiobacilli are capable of autotrophic growth in simple salt media containing a reduced inorganic sulphur compound (such as thiosulphate, $S_2O_3^{2-}$) as electron donor and carbon dioxide as a sole carbon source.

Although autotrophic by nature, facultative forms of thiobacilli capable of adaptation to a heterotrophic environment have been described, according to Trudinger (28). Furthermore, according to Vishniac and Santer (32), the respiration rate of thiobacilli is influenced by the addition of succinate or several other members of the tricarboxylic acid cycle, and glucose.

3.1 Reactions

3.1.1 Oxidation of thiosulphate

Thiosulphate is oxidized to sulphate by all species and strains of thiobacilli which have been studied, according to Trudinger (28).

The overall equation for thiosulphate oxidation is given from (28) as

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+ + 2H + 211 \text{ kcal} \qquad (13)$$

Graham (11) also states an identical equation.

Complete oxidation of thiosulphate to sulphate, however, does not always occur and intermediate products of thiosulphate oxidation, the polythionates, are often formed.

Factors affecting the extent of thiosulphate oxidation to sulphate, (28), are pH, bacterial concentration, amount of aeration, substrate concentration, the partial pressure of oxygen in the gas phase and the absence or presence of phosphate.

3.1.2 Production of polythionates during thiosulphate oxidation

The oxidation of thiosulphate by thiobacilli is characterized by the formation of polythionates, the main ones being trithionate ($S_3O_6^{2-}$), tetrathionate ($S_4O_6^{2-}$) and pentathionate ($S_5O_6^{2-}$). A listing of polythionates formed from thiosulphate by various thiobacilli is presented in Table 11-A.

TABLE 11 - A

PRODUCTION OF POLYTHIONATES FROM THIOSULPHATE BY THIOBACILLI, AFTER TRUDINGER (28)

Organism	Preparation	Polythionates detected
T. thioparus	cultures	trithionate, tetrathionate, pentathionate
	washed bacteria	trithionate, tetrathionate, pentathionate
	extracts	trithionate, tetrathionate
T. thiooxidans	cultures	tetrathionate
	extracts	trithionate, tetrathionate
T. neapolitanus	cultures	trithionate
	washed bacteria	trithionate, tetrathionate, pentathionate
	extracts	tetrathionate

The extent of polythionate accumulation, however, varies widely and depends on a number of experimental factors.

Specific illustrations are from Santer et al., (21) who reported that polythionates accumulated only in the absence of inorganic phosphate and from Jones and Happold (33) who reported the suppression of polythionate formation from thiosulphate by high phosphate concentrations.

The main polythionate which accumulates during thiosulphate oxidation is tetrathionate (28,32). Its formation has been proposed to be due to the direct oxidation of thiosulphate

$$2\,{}^{-}SSO_3^{-} + H_2O + O \rightarrow {}^{-}O_3SSSSO_3^{-} + 2\,OH^{-} \qquad (14)$$

and tetrathionate is the first polythionate detected during thiosulphate oxidation by T.thiooxidans, T.thioparus and T.neapolitanus.

Secondary polythionates formed during thiosulphate oxidation are trithionate and pentathionate. These generally accumulate in small amounts but, under some conditions, they may be the main polythionates formed during the growth of T.thioparus (28).

The formation of trithionate and pentathionate according to Trudinger (28) has been proposed to arise by the chemical disproportionation of tetrathionate, which is enhanced in the presence of thiosulphate and which is thought to result from two nucleophilic displacement reactions according to equations (15) and (16)

$${}^{-}O_3SSSSO_3^{-} + {}^{-}SSO_3^{-} \rightarrow {}^{-}O_3SSSSSO_3^{-} + SO_3^{2-} \qquad (15)$$

$$^{-}O_3SSSSO_3^{-} + SO_3^{2-} \rightarrow {}^{-}O_3SSSO_3^{-} + {}^{-}SSO_3^{-} \qquad (16)$$

Two alternative hypothesis for the formation of trithionate have been advanced (28). The first involves an oxidative reaction between sulphite and thiosulphate

$$SO_3^{2-} + SSO_3 \xrightarrow{2e^{-}} {}^{-}O_3SSSO_3^{-} \qquad (17)$$

The second involves an enzymic reaction between thiosulphate and tetrathionate to give trithionate and a mercapto-thiosulphate ($^{-}SSSO_3^{-}$), equation (18), with subsequent oxidation of the mercapto-thiosulphate to a second molecule of trithionate, equation

$$SSO_3^{2-} + {}^{-}O_3SSSSO_3^{-} \rightarrow {}^{-}O_3SSSO_3^{-} + {}^{-}SSSO_3^{-} \qquad (18)$$

$$^{-}SSSO_3^{-} + \frac{3}{2}O_2 \rightarrow {}^{-}O_3SSSO_3^{-} \qquad (19)$$

However, no direct evidence for reactions (18) and (19) has been reported (28).

3.1.3 Formation of elemental sulphur and sulphate from thiosulphate

The formation of elemental sulphur, a common product of thiosulphate metabolism accumulating outside the bacterial cell and arising from the divalent group of thiosulphate, is governed by experimental conditions (28). Increases in substrate concentration and limitation of the oxygen supply will increase the amounts of sulphur formed, whereas with appropriate pH control, aeration and substrate concentration, thiosulphate is oxidized to sulphate without significant sulphur formation (28).

Sulphur production has been attributed to the extracellular decomposition of pentathionate equation(20) which was assumed to arise from tetrathionate, equation (15)

$$^{-}O_3SSSSSO_3^{-} \rightarrow {}^{-}O_3SSSSO_3^{-} + S^{o} \qquad (20)$$

This decomposition is accelerated by the presence of thiosulphate (28).

Other investigators attribute sulphur formation to specific biological reactions and there is evidence indicating that mechanisms other than pentathionate decomposition operate (28).

Sulphate, the final oxidation of thiosulphate, is formed by T.thioparus to an equal extent from both the sulphur groups of thiosulphate (28). Some studies indicate that there is a preferential conversion of the hexavalent sulphur to sulphate (28). Other studies, however, indicate that the ratio of sulphate formed from the hexavalent sulphur group to that formed from the divalent group is 2:1, with the remaining divalent sulphur converted to elemental sulphur or to the hexavalent sulphur groups of thiosulphate and polythionates (28).

3.2 Reaction Rates

As the purposes of this report were to investigate the effects of influent phosphorous and retention time on thiosulphate oxidation using acclimatized activated sludge, the minimum amount of phosphorous and nitrogen to be added to the influent for both studies sufficient for bacterial growth and energy requirements had first to be determined.

The amount of phosphorous and nitrogen to be added, however, depend on specific growth coefficients for the bacteria, and an explanation leading to their determination is first required.

The starting points are the empirically developed relationships between biological growth and substrate utilization, summarized in two basic equations from Lawrence and McCarty (30).

The first equation describes the relationship between the net rate of growth of microorganisms and substrate utilization,

$$r_x = -Yr_s - bX \qquad (21)$$

where

r_x = net volumetric growth rate of microorganisms, $(\frac{M}{{}^{3}\,{}^{-T}})$

Y = growth yield coefficient, mass of microorganisms/ mass of substrate, $(\frac{M}{M})$

r_s = volumetric reaction rate of substrate by microorganisms, $(\frac{1}{T})$

b = cell-decay coefficient, $(\frac{1}{T})$

X = concentration of microorganisms $(\frac{M}{L^3})$

The second equation relates the volumetric reaction rate of substrate to both the concentration of microorganisms in the reactor and to the substrate surrounding the microorganims,

$$r_s = - [\frac{kSX}{K_s+S}] \tag{22}$$

where

k = maximum rate of substrate utilization per unit weight of microorganisms, $(\frac{1}{T})$

S = concentration of substrate surrounding the microorganisms, $(\frac{M}{L^3})$

K_s = waste concentration at which the rate of waste utilization per unit of microorganisms is half the maximum rate, $(\frac{M}{L^3})$

and the overall negative sign indicates that substrate is disappearing.

The coefficients Y and b relate to bacterial growth and the coefficients k and K_s relate to waste removal (30). In any design, Y and b are necessary whereas k and K_s are not.

3.3 Continuous Flow Reactor Equations

To develop the equations for the minimum amounts of phosphorous and nitrogen to be added to the influent requires the application of equations (1) and (2) from Section 3.2, together with a material balance to the system in question, namely that of a completely mixed reactor without solids recycle.

The material balance equation can be fundamentally stated as

$$\left[{\text{Mass} \atop \text{Reaction Rate}}\right] + \left[{\text{Mass} \atop \text{Input Rate}}\right] = \left[{\text{Mass} \atop \text{Output Rate}}\right] + \left[{\text{Mass} \atop \text{Accumulation Rate}}\right]$$

Under steady state conditions this expression simplifies with the elimination of the mass accumulation rate term.

Performing a material balance for the influent substrate and assuming steady state conditions,

$$Vr_s + Q(S_o) = Q(S) + 0$$

where

V = reactor volume (L^3)

Q = influent flowrate, (L^3/T)

S_o = influent substrate concentration, (M/L^3)

S = effluent substrate concentration, (M/L^3)

Simplifying

$$r_s = -\left[\frac{Q(S_o - S)}{V}\right] \tag{23}$$

However, from equation (20),

$$r_x = -Yr_s - bX$$

therefore, $\frac{r_x}{X} = \frac{-Yr_s}{X} - \frac{bX}{X}$

which reduces to $\frac{r_x}{X} = \frac{-Yr_s}{X} - b$

However, $\frac{r_x}{X} = \frac{1}{\theta_c}$, from the definition of θ_c, the solids retention time (30).

Therefore, $\frac{1}{\theta_c} = \frac{-Yr_s}{X} - b$ (24)

Substituting equation (23) into (24),

$$\frac{1}{\theta_c} = \frac{Y}{X}[\frac{Q(S_o-S)}{V}] - b$$

and $XV = \frac{YQ\theta_c(S_o-S)}{(1+b\theta_c)}$

Thus, $X = \frac{YQ\theta_c(S_o-S)}{V(1+b\theta_c)}$

However, $\frac{Q}{V} = \frac{1}{\theta}$ where θ is the hydraulic retention time, and for a completely mixed reactor without recycle is identical to θ_c, the solids retention time.

Thus, $X = \frac{Y(S_o-S)}{(1+b\theta_c)}$

The amount of phosphorous to be supplied is given from (30) as

$$P_p = 0.024(P_x)$$

where P_p = daily phosphorous requirement, (M/T)

P_x = sludge production rate, (M/T)

and $P_x = \frac{YQ(S_o-S)}{(1+b\theta_c)}$

The nitrogen requirement is given as

$$P_N = 0.12(P_x)$$

where P_N = daily nitrogen requirement, (M/T)

It remains, therefore to determine values for the coefficients Y and b.

3.4 Coefficient Values

The coefficients Y and b must be known before the minimum daily requirements for phosphorous and nitrogen can be determined.

3.4.1 Determination of Y

The cell yield coefficient Y was determined from thermodynamic considerations using a procedure outlined by Christensen and McCarty (31).

This procedure has its basis in oxidation half-reactions for electron donors and electron acceptors. Table 12 is a summary of oxidation half-reactions from (31) required for the determination of Y.

The procedure to determine Y, for the purposes of this report, is summarized as follows. It is to be remarked at the outset, however, that the summarized procedure is not exhaustive and the reader is referred to the paper of Christensen and McCarty (31) for a more thorough explanation.

Before a value of Y can be obtained, it is necessary, first, to determine the value of a_s, a form of growth yield coefficient, and the precursor of Y, from

$$a_s = [\frac{1}{1+A}]$$

in which

$$A = -[\frac{\Delta G_p/n^m + \Delta G_n/n + 7.5}{n\Delta G_r}]$$

It then becomes a matter of substituting the terms in the above expression for A.

TABLE 12

OXIDATION HALF-REACTIONS after (31).

Reaction Number	Half-Reactions		$\Delta G^{\circ}(W)$ (kcal/electron equivalent)
	Reactions for bacterial cell synthesis (R_c):		
	Ammonia as nitrogen source:		
1	$\frac{1}{20}C_5H_7O_2N + \frac{9}{20}H_2O$	$= \frac{1}{5}CO_2 + \frac{1}{20}HCO_3^- + \frac{1}{20}NH_4^+ + H^+ + e^-$	
	Nitrate as nitrogen source:		
2	$\frac{1}{28}C_5H_7O_2N + \frac{11}{28}H_2O$	$= \frac{1}{28}NO_3^- + \frac{5}{28}CO_2 + \frac{29}{28}H^+ + e^-$	
	Reactions for electron acceptors (R_a):		
	Oxygen:		
3	$\frac{1}{2}H_2O$	$= \frac{1}{4}O_2 + H^+ + e^-$	18.675
	Nitrate:		
4	$\frac{1}{10}N_2 + \frac{3}{5}H_2O$	$= \frac{1}{5}NO_3^- + \frac{6}{5}H^+ + e^-$	17.128
	Sulfate:		
5	$\frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	$= \frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^-$	−5.085
	Carbon dioxide (methane fermentation):		
6	$\frac{1}{8}CH_4 + \frac{1}{4}H_2O$	$= \frac{1}{8}CO_2 + H^+ + e^-$	−5.763
	Reactions for electron donors (R_d):		
	Organic donors (heterotrophic reactions):		
	Domestic Wastewater:		
7	$\frac{1}{50}C_{10}H_{19}O_3N + \frac{9}{25}H_2O$	$= \frac{9}{50}CO_2 + \frac{1}{50}NH_4^+ + \frac{1}{50}HCO_3^- + H^+ + e^-$	−7.6
	Protein (amino acids, proteins, nitrogenous organics):		
8	$\frac{1}{66}C_{16}H_{24}O_5N_4 + \frac{27}{66}H_2O$	$= \frac{8}{33}CO_2 + \frac{2}{33}NH_4^+ + \frac{31}{33}H^+ + e^-$	−7.7
	Carbohydrate (cellulose, starch, sugars):		
9	$\frac{1}{4}CH_2O + \frac{1}{4}H_2O$	$= \frac{1}{4}CO_2 + H^+ + e^-$	−10.0
	Grease (fats and oils):		
10	$\frac{1}{46}C_8H_{16}O + \frac{15}{46}H_2O$	$= \frac{4}{23}CO_2 + H^+ + e^-$	−6.6
	Acetate:		
11	$\frac{1}{8}CH_3COO^- + \frac{3}{8}H_2O$	$= \frac{1}{8}CO_2 + \frac{1}{8}HCO_3^- + H^+ + e^-$	−6.609
	Propionate:		
12	$\frac{1}{14}CH_3CH_2COO^- + \frac{5}{14}H_2O$	$= \frac{1}{7}CO_2 + \frac{1}{14}HCO_3^- + H^+ + e^-$	−6.664
	Benzoate:		
13	$\frac{1}{30}C_6H_5COO^- + \frac{19}{30}H_2O$	$= \frac{1}{5}CO_2 + \frac{1}{30}HCO_3^- + H^+ + e^-$	−6.892
	Ethanol:		
14	$\frac{1}{12}CH_3CH_2OH + \frac{1}{4}H_2O$	$= \frac{1}{6}CO_2 + H^+ + e^-$	−7.592
	Lactate:		
15	$\frac{1}{12}CH_3CHOHCOO^- + \frac{1}{3}H_2O$	$= \frac{1}{6}CO_2 + \frac{1}{12}HCO_3^- + H^+ + e^-$	−7.873
	Pyruvate:		
16	$\frac{1}{10}CH_3COCOO^- + \frac{2}{5}H_2O$	$= \frac{1}{5}CO_2 + \frac{1}{10}HCO_3^- + H^+ + e^-$	−8.545
	Methanol:		
17	$\frac{1}{6}CH_3OH + \frac{1}{6}H_2O$	$= \frac{1}{6}CO_2 + H^+ + e^-$	−8.965
	Inorganic donors (autotrophic reactions):		
18	Fe^{2+}	$= Fe^{3+} + e^-$	17.780
19	$\frac{1}{8}NH_4^+ + \frac{3}{8}H_2O$	$= \frac{1}{8}NO_3^- + \frac{5}{4}H^+ + e^-$	8.245
20	$\frac{1}{6}NH_4^+ + \frac{1}{3}H_2O$	$= \frac{1}{6}NO_2^- + \frac{4}{3}H^+ + e^-$	7.852
21	$\frac{1}{6}S + \frac{2}{3}H_2O$	$= \frac{1}{6}SO_4^{2-} + \frac{4}{3}H^+ + e^-$	−4.657
22	$\frac{1}{16}H_2S + \frac{1}{16}HS^- + \frac{1}{2}H_2O$	$= \frac{1}{8}SO_4^{2-} + \frac{19}{16}H^+ + e^-$	−5.085
23	$\frac{1}{8}S_2O_3^{2-} + \frac{5}{8}H_2O$	$= \frac{1}{4}SO_4^{2-} + \frac{5}{4}H^+ + e^-$	−5.091
24	$\frac{1}{2}H_2$	$= H^+ + e^-$	−9.670
25	$\frac{1}{2}SO_3^{2-} + \frac{1}{2}H_2O$	$= \frac{1}{2}SO_4^{2-} + H^+ + e^-$	−10.595
	Custom reaction for unknown organics:		
26	$C_aH_bO_cN_d + (2a - c)H_2O$	$= aCO_2 + dNH_4^+ + (4a + b - 2c - 4d)H^+ + (4a + b - 2c - 3d)e^-$	

The term ΔG_p represents the energy required to convert the cell carbon source to an intermediate stage. For inorganic electron donors, see reaction (23), Table 12.

$$\Delta G_p = +27.22 \text{ kcal/electron equivalent}$$

The value of m is (+1) if ΔG_p is positive. The value of n represents the efficiency of energy transfer and is taken to equal 0.6.

The term ΔG_n represents the energy to convert the nitrogen source for cell synthesis into ammonia. In this study, ammonium nitrate (NH_4NO_3) was used as the nitrogen source and accordingly,

$$\Delta G_n = 0$$

The term $\Delta G_r = [\Delta G^\circ(W)_d - \Delta G^\circ(W)_a]$ in which $\Delta G^\circ(W)_d$ and $\Delta G^\circ(W)_a$ are the reaction energies for the electron donor and electron acceptor, respectively, in kcal/electron equivalent.

The electron donor is the inorganic thiosulphate anion, $S_2O_3^{2-}$, and from reaction (23), Table 12,

$$\Delta G^\circ(W)_d = -5.091 \text{ kcal/electron equivalent}$$

The electron acceptor is oxygen, O_2, (for aerobic processes), and from reaction (3), Table 12,

$$\Delta G^\circ(W)_a = +18.675 \text{ kcal/electron equivalent}$$

Thus, $\Delta G_r = [-5.091 - 18.675]$

therefore, $\Delta G_r = -23.766$ kcal/electron equivalent.

Substituting into the above express for A,

$$A = -\left[\frac{\frac{27.22}{(0.6)^{+1}} + 0 + 7.5}{0.6(-23.766)}\right]$$

Thus, $A = +3.687$

Since $a_s = \frac{1}{1+A}$

Therefore, $a_s = 0.213 \frac{\text{equivalents cell}}{\text{equivalents donor}}$

The value for a_s is converted to Y by multiplying by the conversion factor (113/r). Since ammonia (as ammonium nitrate) was used as the nitrogen source, from reaction (1), Table 12 , r = 20.

Thus, momentarily,

$$Y = 0.213 \frac{\text{equivalents cell}}{\text{equivalents donor}} \times \frac{113\ \text{g.cell}}{20\ \text{equivalents cell}}$$

An additional conversion factor is based on reaction (23), Table

$$1/8\ S_2O_3^{2-} + 5/8\ H_2O = 1/4\ SO_4^{2-} + 5/4\ H^+ + e^-$$

which indicates that 1 molecule of $S_2O_3^{2-}$ oxidized donates 8 electrons. The formula weight for $S_2O_3^{2-}$ is 112 g.

Thus, there are 112 g $S_2O_3^{2-}$/8 electrons, and the value for Y is,

$$Y = 0.213 \frac{\text{equiv. cell}}{\text{equiv. donor}} \times \frac{113\ \text{g. cell}}{20\ \text{equiv. cell}} \times \frac{8\ \text{electrons}}{112\ \text{g}\ S_2O_3^{2-}\ \text{oxidized}}$$

$$Y = 0.086 \frac{\text{mg cell}}{\text{mg}\ S_2O_3^{2-}}$$

3.4.2 Determination of b

The cell-decay coefficient b was taken to be 0.07/day from a report by Kreye _et al_., (14,15) after first re-interpreting their notation into the notation used by Lawrence and McCarty (30). A comment on the appropriateness of this value of b is given by Christensen and McCarty (31), who state that appropriate values to use at 20°C for b would be 0.05/day for autotropic systems and 0.20/day for aerobic heterotrophic systems.

3.4.3 Determination of k and K_s

Estimates of appropriate values for these coefficients for thiosulphate oxidizing systems could not be obtained from the results of Kreye _et al_., (14,15).

For the coefficient k, Christensen and McCarty (31) state that:

> "the value of k is about the same for all bacteria for a given temperature when k is expressed in terms of electron equivalents converted to energy per day per grain of bacteria."

and provide an expression for the determination of k as:

$$k = 86.7(10)^7 \exp(-12{,}000)/1.99(T + 273)$$

where T = temperature, °C.

At 20°C, k is 1.0 electron equivalents/day/g bacteria.

For the coefficient K_s, Christensen and McCarty (31) state that:

> "the most uncertain coefficient is K_s ..... little fundamental knowledge is available to help in the selection of appropriate values so reliance must be placed on empirical observations."

It should be remarked, that the coefficients k and K_s were not required for this report.

CHAPTER 4

THE EXPERIMENTS

4.1 Nutritional Requirements

With values of (Y) and (b) it is then possible to obtain the phosphorous requirement (Pp) for both studies.

The following information is common to both studies

$Y = 0.086$ mg $S_2O_3^{2-}$/mg cell

$b = 0.07$ day^{-1}

So = Influent thiosulphate concentration.

The source of thiosulphate for both studies was synthetically prepared from sodium thiosulphate with five waters of hydration ($Na_2S_2O_3.5H_2O$, Formula weight = 248). A concentration of 2000 mg/l $Na_2S_2O_3.5H_2O$ was used supplying theoretically* 904 mg/l of thiosulphate anion. Thus, the influent thiosulphate concentration (So) was 904 mg/l for both studies.

4.1.1 Influent Phosphorous Variation Study

The following is known

$Y = 0.086$ mg $S_2O_3^{2-}$/mg cell

$b = 0.07$ day^{-1}

Sо = 904 mg/l thiosulphate

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*Ratio of $Fw(S_2O_3^{2-})/Fw(Na_2S_2O_3.5H_2O) = \frac{112}{248} = 0.452$

$S = 0$ mg/1 (assume no thiosulphate in effluent as best case study)

$\theta_c = 3$ days

$Q = 1$ 1/day, influent flowrate

therefore, $X = \frac{Y(So - S)}{1 + b\theta_c} = 57.6$ mg/1

$P_x = Q(X) = 1$ 1/day (57.6 mg/1) = 57.6 mg/1day

$P_p = 0.024(P_x) = 0.024$ (57.6 mg/day) = 1.38 mgP/day.

As the purpose of this study was to determine the effect of different phosphorous concentrations on thiosulphate oxidation, three reactors were used each supplied with different amounts of phosphorous in the influent.

Reactor (1) was supplied with 3.0 mg/1P (greater than the calculated phosphorous requirement by a factor of 2.2), Reactor (2) with 9.8 mg.1P (greater than the calculated phosphorous requirement by a factor of 7.1) and Reactor (3) with 16.6 mg/1P (greater than the calculated phosphorous requirement by a factor of 12.0)

A 10 g/1 stock solution of potassium di-hydrogen phosphate (KH_2PO_4) was used as the source of phosphorous. The daily phosphorous requirement for Reactors (1), (2) and (3) was, respectively, 1.6 ml, 4.3 ml and 8.3 ml of KH_2PO_4 stock solution per litre of influent.

The daily requirement for the other main nutrient, nitrogen, was calculated from

$P_N = 0.12 (P_x) = 0.12$ (57.6) = 6.9 mgN/day and supplied by ammonium nitrate (NH_4NO_3, FW = 80). Thus,

$$6.9 \frac{\text{mg N}}{\text{day}} \times 2.86 \frac{\text{mgNH}_4\text{NO}_3}{\text{mgN}} = 19.7 \frac{\text{mgNH}_4\text{NO}_3}{\text{day}}$$

This daily requirement was provided by 10 ml of a 20 g/l NH_4NO_3 stock solution per litre of influent supplying 200 mg of NH_4NO_3 per litre. The same amount of NH_4NO_3 was added to each reactor. Excess nitrogen was supplied as a limitation of this nutrient had to be avoided.

Trace elements were supplied from a stock solution, the composition which was:

$MgSO_4 \cdot 7H_2O$	15.0 g	Dissolved in 2 ℓ distilled water
$ZnSO_4 \cdot 7H_2O$	0.5 g	
$FeSO_4 \cdot 7H_2O$	0.5 g	
$MnSO_4 \cdot 3H_2O$	0.5 g	
$CaCl_2$	2.0 g	

Ten ml of trace element stock solution per litre of influent was considered to provide a sufficient supply of trace elements.

Table 13 provides a complete summary of the influent characteristics flowrates and retention times for this study.

4.1.2 Retention Time Variation Study

The conditions under which this study was conducted were similar to the phosphorous variation study, with the exception that the solid retention time (θ_c) was varied, each reactor operating with a different (θ_c). Performance of each reactor was monitored until

TABLE 13 SUMMARY OF INFLUENT CHARACTERISTICS FOR THE INFLUENT PHOSPHOROUS VARIATION STUDY

Reactor No.	Influent $Na_2S_2O_3 \cdot 5H_2O$ Concentration (mg/l)	Influent $S_2O_3^{2-}$ concentration (mg/l)	Daily P Requirement (mg/day)	Daily P[1] Supply (mg/day)	Ratio of P Supply/ P Requirement	Daily N Requirement (mg/day)	Daily N[2] Supply (mg/day)	Daily Trace Element Supply[3] (ml)	Reactor Volume (l)	θc (days)	Q (l/day)
1	2000	904	1.38	3.0	2.2	6.9	200	10	5	5	1
2	2000	904	1.38	9.8	7.1	6.9	200	10	5	5	1
3	2000	904	1.38	16.6	12.0	6.9	200	10	5	5	1

[1] Supplied from a 10 g/l KH_2PO_4 stock solution

[2] Supplied from a 20 g/l NH_4NO_3 stock solution

[3] Supplied from a Trace Element stock solution, the composition of which is outlined in the text.

steady-state conditions prevailed or until reactor failure occurred.

Influent characteristics were held constant, and phosphorous, nitrogen and trace elements came from the same strength stock solutions as used in the phosphorous variation study. The amounts of stock solution added were the same, with the only exception that 4.3 ml KH_2PO_4 stock solution per litre of influent was supplied to each reactor.

The retention time was varied by adjusting the flowrate in accordance with the equation

$$\theta = \frac{V}{Q}$$

where θ = hydraulic (or solids) retention time (days)

V = volume of reactor (5 l)

Q = influent flowrate (l/day)

Table 14 provides a summary of the influent characteristics flowrates and retention times for the retention time variation study.

4.2 Experimental Procedures

The general approach to this study was to acclimatize activated sludge to increasing concentrations of thiosulphate by a fill-and-draw process, and when sufficiently acclimatized to transfer the activated sludge to a continuous flow reactor of pre-established volume without solids recycle, i.e., a simulated aerated lagoon, whereupon an influent containing a constant concentration of thiosulphate, along with nitrogen, phosphorous and trace elements would be supplied.

TABLE 14 SUMMARY OF INFLUENT CHARACTERISTICS FOR THE RETENTION TIME VARIATION STUDY

Reactor No.	Reactor Volume (l)	θ_r (days)	Q (l/day)	Influent $Na_2S_2O_3 \cdot 5H_2O$ concentration (mg/l)	Influent S_2O_3 concentration (mg/l)	Daily P Requirement (mg/day)	Daily P[1] Supply (mg/day)	Daily N Requirement (mg/day)	Daily N[2] Supply (mg/day)	Daily Trace Element Supply[3] (ml)
1	5	4	1.25	2000	904	1.38	9.8	6.9	200	10
2	5	3	1.67	2000	904	1.38	9.8	6.9	200	10
3	5	2	2.5	2000	904	1.38	9.8	6.9	200	10
1	5	½	10	2000	904	1.38	9.8	6.9	200	10
2	5	1	5	2000	904	1.38	9.8	6.9	200	10
3	5	¼	20	2000	904	1.38	9.8	6.9	200	10

[1] Supplied from a 10 g/l KH_2PO_4 stock solution

[2] Supplied from a 20 g/l NH_4NO_3 stock solution

[3] Supplied from a Trace Element stock solution, the composition of which is outlined in the text.

4.2.1 Acclimation and Start-Up

Activated sludge was obtained from the sludge recycle line at Watts Creek Sewage Treatment Plant, Ottawa, placed in two 5 litre batch reactors and aerated. Initial microscopic observations revealed the presence of microorganisms common to activated sludge, especially rotifers. No rod-shaped bacteria typical of the genus Thiobacillus were observed. The initial pH of the activated sludge was 7.2.

Acclimatization was performed on a fill-and-draw basis. First, aeration was stopped allowing the sludge solids to settle whereupon a volume of effluent was withdrawn. This was replaced by an equivalent volume of synthetic feed consisting of thiosulphate in the form $Na_2S_2O_3$, at first in low concentrations (100 mg/l) and then in higher concentrations (2000 mg/l). With each addition of thiosulphate, nitrogen, phosphorous and trace elements were also added.

To monitor the efficacy of the acclimatization process, daily pH and MLVSS determinations were taken.

Tables 15 and 16 and Figures 1 and 2 document the change of MLVSS and pH with time during acclimzation for batch reactors (1) and (2) respectively.

Periodically Thiobacillus thiooxidans, a thiosulphate oxidizing species of bacteria, was added to the mixed liquor to hasten the acclimatization when it was observed that after the first twenty days or so, the pH had been reduced very little. A low pH is indicative of efficient thiosulphate oxidation when T. thiooxidans is used.

TABLE 15 Change of MLVSS During Acclimatization Period for Batch Reactor (I)

DAY	MLVSS (mg/l)	DAY	MLVSS (mg/l)	DAY	MLVSS (mg/l)
1	---	24	740	47	600
2	---	25	---	48	470
3	2320	26	990	49	570
4	1100	27	810	50	440
5	1400	28	890	51	460
6	1070	29	---	52	410
7	---	30	---	53	420
8	---	31	730	54	440
9	---	32	730	55	480
10	1120	33	800	56	320
11	---	34	---	57	370
12	960	35	760	58	---
13	---	36	---	59	320
14	---	37	520	60	380
15	---	38	---	61	300
16	840	39	420	62	---
17	---	40	470	63	310
18	---	41	520	64	300
19	---	42	560	65	---
20	1000	43	530	66	---
21	---	44	---	67	---
22	---	45	580	68	320
23	---	46	630		

TABLE 16 Change of MLVSS During Acclimatization Period for Batch Reactor (2)

DAY	MLVSS (mg/l)	DAY	MLVSS (mg/l)	DAY	MLVSS (mg/l)
1	---	24	720	47	610
2	---	25	---	48	480
3	1949	26	720	49	570
4	1360	27	720	50	460
5	1230	28	810	51	440
6	820	29	---	52	410
7	---	30	---	53	340
8	---	31	710	54	380
9	---	32	660	55	440
10	870	33	690	56	300
11	---	34	---	57	350
12	830	35	680	58	---
13	---	36	---	59	320
14	---	37	560	60	360
15	---	38	---	61	310
16	670	39	450	62	---
17	---	40	470	63	320
18	---	41	510	64	310
19	---	42	540	65	---
20	850	43	550	66	---
21	---	44	---	67	---
22	---	45	510	68	310
23	---	46	560		

Figure (1). pH change during acclimatization period for batch reactor 1.

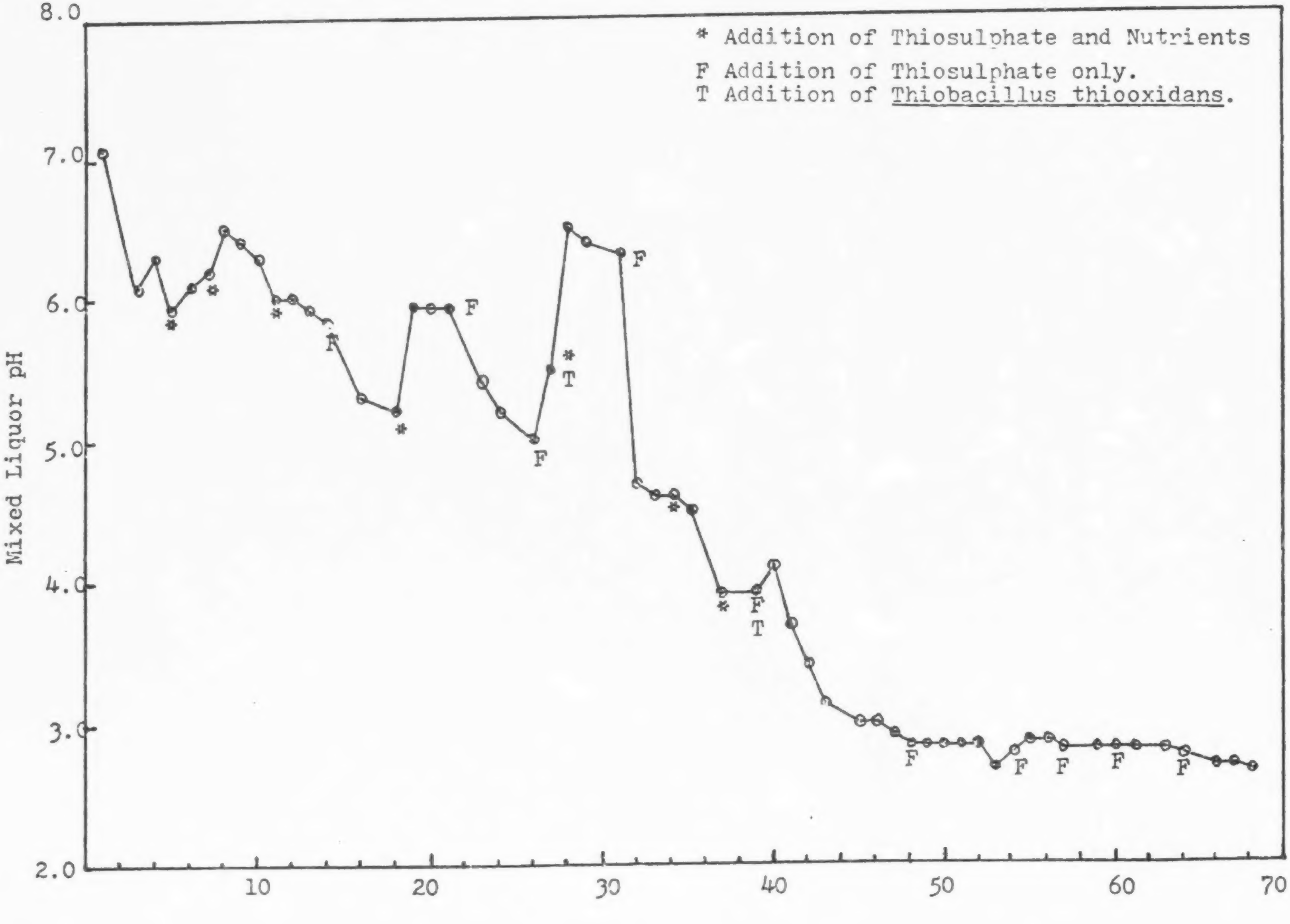
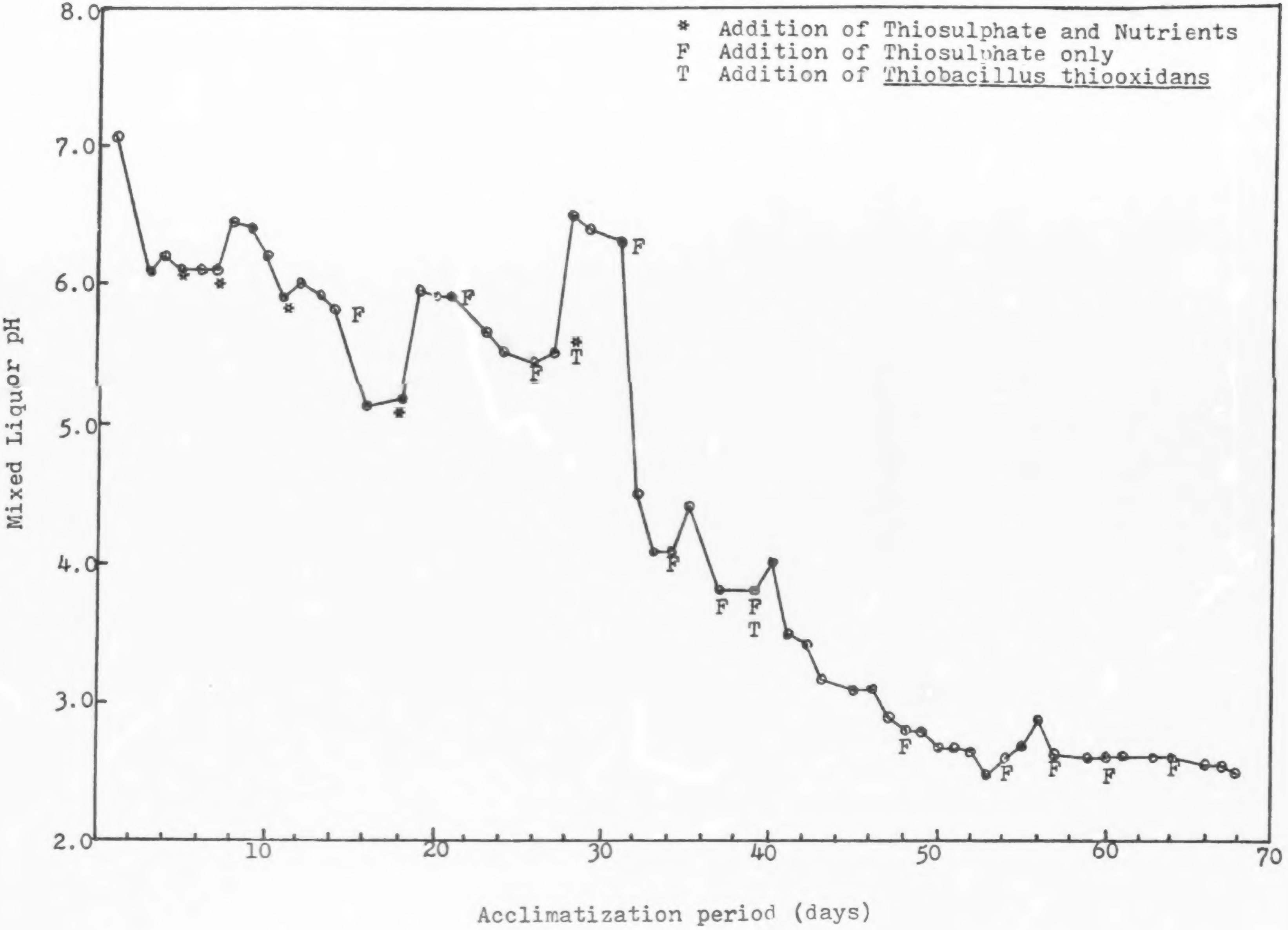


Figure (2). pH change during acclimatization period for batch reactor 2.



This addition can be questioned, but the reasons for adding T. thiooxidans are several, and considered to be valid.

(a) According to the literature (3),(22) and to work performed at the Canada Centre for Inland Waters (CCIW), Burlington, Ontario, effluent thiosulphate oxidation can be accomplished biologically using certain members of the genus Thiobacillus.

(b) T. thiooxidans is an acidophilic species, thus when sulphate and hydrogen ions are produced during thiosulphate oxidation, the resulting decrease in pH is to the advantage of this species whereas for others it is not.

(c) With T. thiooxidans preferring an acid medium, no pH control is necessary to maintain the pH at the neutral point as is required for some other species of Thiobacillus.

(d) T. thiooxidans was the only thiosulphate oxidizing species available from the National Research Council (NRC) Culture Collection, 100 Sussex Drive, Ottawa, Ontario.

The effect of T. thiooxidans addition can be noticed in Figures 1 and 2 From these figures the following can be noted:

(a) A marked reduction of pH after the two additions of T. thiooxidans.

(b) An initial lag effect before the pH decreases.

(c) A progressive decreas in MLVSS as acidity increases (i.e., pH decreases). This acidity increase can be attributed to thiosulphate oxidation to sulphate by T. thiooxidans.

Microscopic examinations were made as the pH decreased, and it was observed that the rotifers were dying off to be replaced by small rod shaped organisms characteristic of T. thiooxidans. With this decrease in pH and MLVSS the turbidity and colour of the mixed liquor changed from that of activated sludge (VSS = 2400 mg/l) to a much paler solution (VSS $\approx$ 300 mg/l).

Acclimatization was continued using the fill-and-draw process until the pH decreased to the optimum range for T. thiooxidans around pH 2.5 to 3.0, whereupon the contents of the two 5 litre reactors (10 litres in total) were transferred to three 5 litre complete mix reactors without recycle, resulting in a dilution and proportioning of the 10 litre of acclimatized mixed liquor to approximately 10/3 or 3.33 litre of mixed liquor in each reactor.

The reactor contents were then brought up to 5.0 litres by feeding a solution consisting of thiosulphate (at 2000 mg/l), nitrogen, phosphorous and trace elements at a flowrate of 1 l/day. During the feeding, the reactor contents were aerated. When the 5 litre mark was reached, influent pumping was stopped, the effluent pipe was covered and the reactor contents were further aerated for five days, the purpose of which was to minimize the affects of dilution.

After five days, influent pumping was restarted and continuous flow operation commenced.

It should be noted that due to reactor failure during the first phosphorous variation study, and similar reactor failure during the first retention time variation study (thought to be due to heavy metal contamination in both cases) two reactors were rendered void and as the results were unsatisfactory, one remaining reactor (5 1) had to be used to restart the two failed reactors as sufficient data had yet to be collected. This restarting was accomplished in the following manner.

Five litres of mixed liquor was divided between two reactors providing 2.5 1/reactor. This was diluted to 3.0 1 with tap water and 5 mls of an active T. thiooxidans cuture were added to each reactor. Influent with, at first, 1000 mg/1 then later 2000 mg/1 thiosulphate, nitrogen, excess phosphorous and trace elements were supplied at a flowrate of 1 1/day.

The initial pH was 2.25, but after transferring and diluting was 2.4. By the fifth day, the mixed liquor pH in both reactors was 2.2, indicating successful acclimatization.

The two acclimatized reactors were then used to restart a third reactor, in a similar manner as described above.

4.2.2 Reactor Assembly and Equipment

The continuous flow reactors used were conventional rectangular bench scale models made, in the workshops, from perspex.

Having decided on a retention time of 5 days and a flowrate of 1 1/day (both maintained throughout the phosphorous ariation study), the reactor volume of 5 1 was obtained by adjusting the length of the effluent pipe.

Influent was stored in a coloured bottle, to minimize thiosulphate decomposition by light, and pumping was performed by a Buchler polystatic pump. All influent feed lines were of new 5/8 inch Tygon tubing and other necessary connections were also of new Tygon tubing.

Aeration was provided with an air stone, after compressed air was first moisturized by passing through a water trap to minimize evaporation losses. As a further precaution against evaporation losses, the reactors were covered with aluminium foil (Reynolds heavy duty foil).

Calibration of the polystatic pumps was achieved by expressing the flowrate of (x)l/day as (y) ml/2 minutes and assuming an influent Specific Gravity of 1.0, i.e., water, re-expressing (y) ml/2 mins as (y) mg/2 mins. The flowrate was then adjusted to provide this weight. It is considered that this method is quite accurate and above all quick, and was used as a daily check on the flowrate.

Figure 3 shows diagramtically the apparatus set up, and Figures 4 to 6 show pictorially the apparatus and its deployment.

4.2.3 Experimental Procedures.

For each study, reactor performances were monitored until about ten days after steady-state, in the case of the phosphorous variation study and the higher retention times, or until reactor failure occurred, in the case of the lower retention times.

To assess the efficiency of the treatment, various parameters relating to the influent, mixed liquor and effluent were monitored daily. Table 17 summarized the analyses performed.

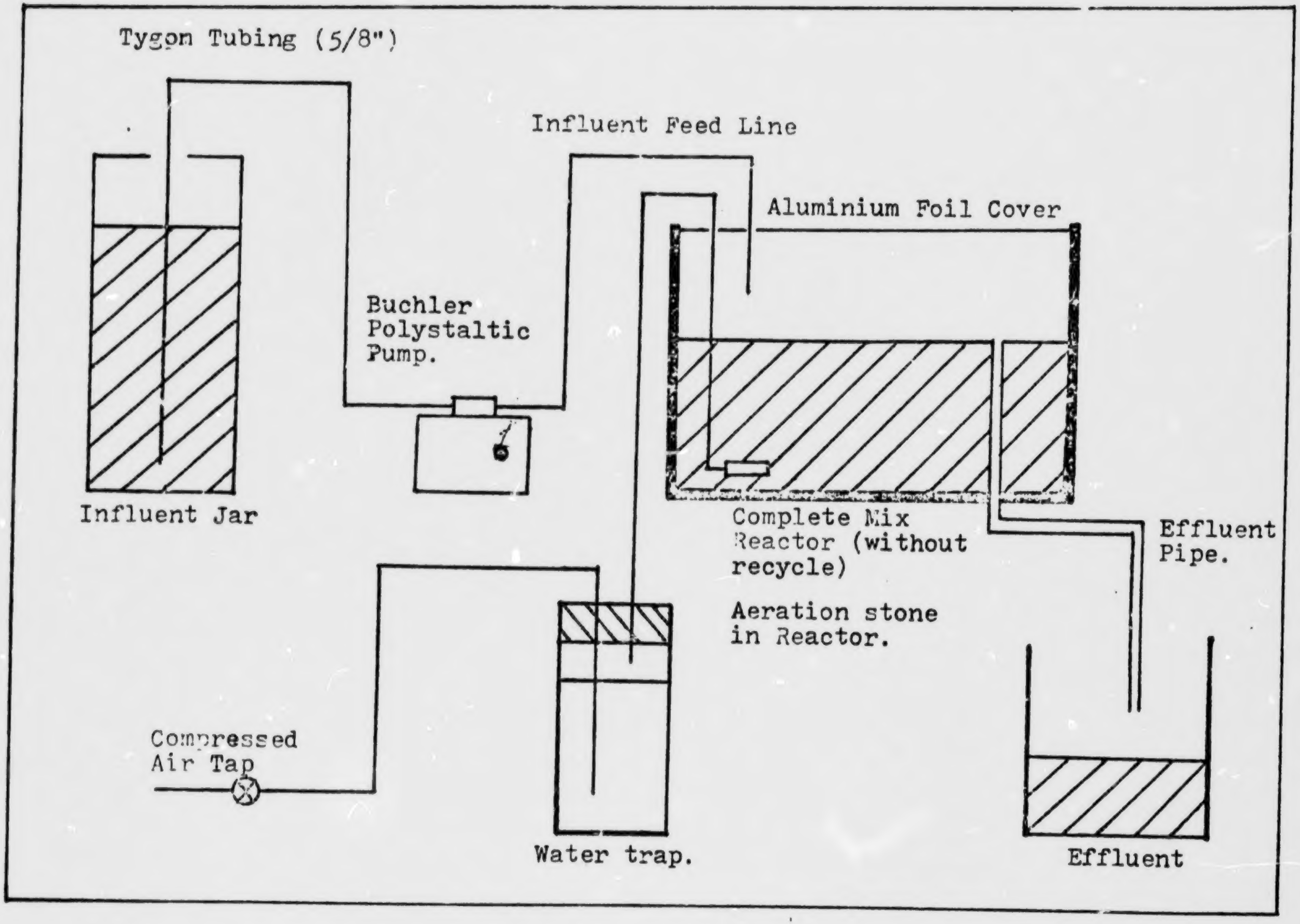

Tygon Tubing (5/8")
Influent Feed Line
Aluminium Foil Cover
Buchler Polystaltic Pump.
Influent Jar
Complete Mix Reactor (without recycle)
Effluent Pipe.
Aeration stone in Reactor.
Compressed Air Tap
Water trap.
Effluent

Figure (3). Diagram of Reactor and Equipment Arrangement.

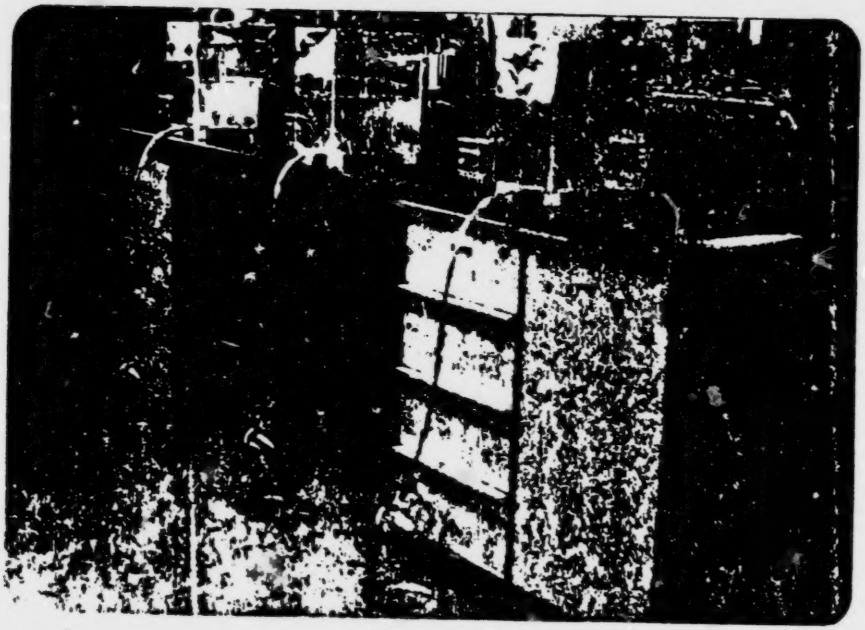


Figure (4). Overall reactor assembly and arrangement for both phosphorous variation and retention time variation studies.

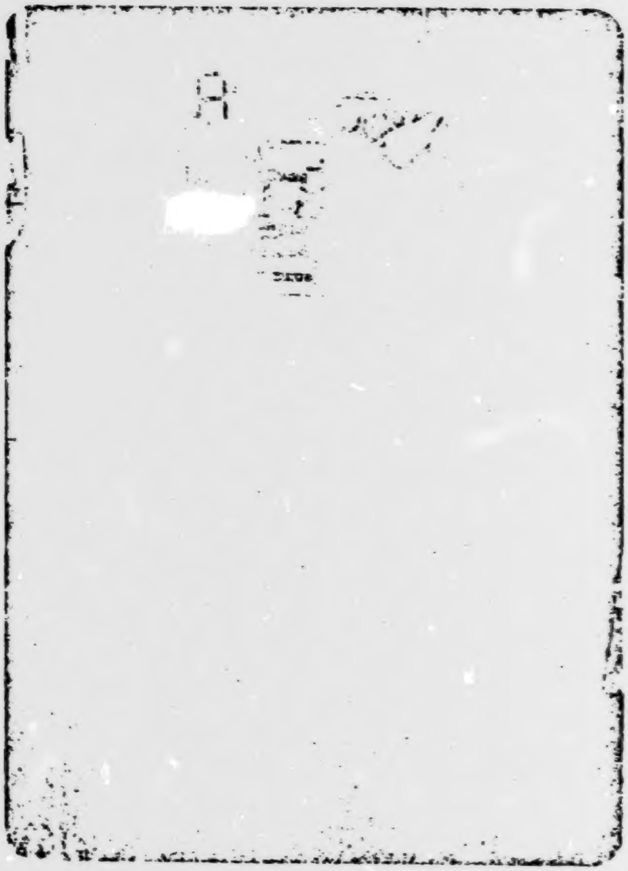


Figure (5). An overall view of the reactor assembly for the biological oxidation of thiosulphate.

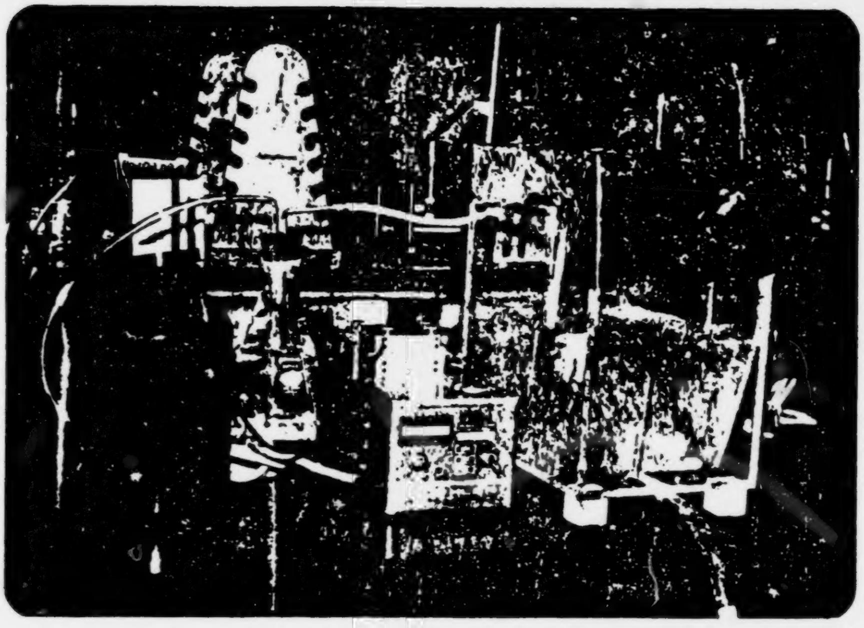


Figure (6). A more detailed view of the reactor of Figure (5).

TABLE 17 LIST OF ANALYSES PERFORMED

Influent	Mixed Liquor	Effluent
(1) Chemical Oxygen Demand (2) Thiosulphate (3) Sulphate* (4) pH	(1) MLTSS (2) MLVSS (3) pH (4) Temperature	(1) Chemical Oxygen Demand (2) Thiosulphate (3) Polythionates (4) Sulphate (5) pH (6) Turbidity

All analyses performed daily unless otherwise indicated.

* Performed only with every feeding.

4.3 Analytical Procedures

A brief summary of the analytical procedures follows.

4.3.1 COD

The procedure outlined in Standard Methods (14th Edition) section 508, page 550 (1) was used.

A mixture of sample, potassium dichromate (0.25 N), sulphuric acid, mercuric sulphate and silver sulphate is refluxed for two hours after which it is cooled to room temperature. Excess dichromate is titrated with Ferrous Ammonium Sulphate (FAS). A similar analysis is performed on a blank consisting of distilled water plus the aforementioned reagents.

The final calculation is given as:

$$\text{COD} = \left[\frac{(a-b)(c)8000}{v}\right] \text{ mg/l}$$

where
a = FAS titrant required for blank
b = FAS titrant required for sample
c = normality of FAS titrant
v = sample volume

This analysis is valid for a COD range from 50 to 2000 mg/l and was used unmodified on the effluent.

The procedure has a standard deviation of ± 10 mg/l.

4.3.2 Thiosulphate

The procedure used is a well established wet chemical analysis and has been used before by the Canada Centre for Inland Waters, Burlington, Ontario (16).

The thiosulphate anion is oxidized to tetrathiorate in weakly acid solution with iodine, according to the reaction:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

Starch is used as the indicator. The procedure has an error of ±5%.

The analytical procedure is summarized as follows:

An appropriate aliquot of sample is pipetted into a beaker (if the $S_2O_3^{2-}$ concentration varies from 100 - 1000 mg/l, use 25 ml aliquot; if from 0 - 100 mg/l, use 50 ml aliquot), and 2 ml of formaldehyde are added for every 1000 mg of sulphite anion present. The sample is then diluted, if necessary, to 50 ml with distilled water, and the pH is adjusted, with a pH meter, to within the range of 4-5 with either 10% HCl or 10% NH_4OH. Five drops of starch are then added, and the sample is then titrated with 0.01 N standardized iodine solution to the first permanent blue colour.

The concentration of thiosulphate is obtained from

$$\text{mg/l } S_2O_3^{2-} = \frac{TN}{A}(112{,}000)$$

where T = ml of iodine titrant used

N = normality of iodine titrant

A = volume of sample used.

4.3.3 Polythionate

The procedure used was from CCIW, Burlington (16). Polythionates, intermediate products of thiosulphate oxidation and containing three, four or five sulphur atoms, react with mercuric chloride to quantitatively release acid in solution. The stoichiometic equation is:

$$2S_nO_6^{2-} + 3HgCl_2 + 4H_2O \rightarrow HgCl_2.2HgS + 8H^+ + 4Cl^- + 4SO_4^{2-} + (2n-6)S$$

A similar equation applies for thiosulphate

$$2S_2O_3^{2-} + 3HgCl_2 + 2H_2O \rightarrow HgCl_2.2HgS + 4H^+ + 4Cl^- + 2SO_4^{2-}$$

In both cases, the acid generated may be titrated with standard caustic solution to determine the concentration of these four sulphur anions:$S_2O_3^{2-}$ (thiosulphate), $S_2O_3^{2-}$ (trithionate), $S_4O_6^{2-}$ (tetrathionate) and $S_5O_6^{2-}$ (pentathionate).

As the concentration of polythionates is expressed as thiosulphate, thiosulphate in the effluent, as determined in section 4.3.2 was subtracted from the polythionate concentration to determine the concentration of $S_3O_6^{2-}$, $S_4O_6^{2-}$ and $S_5O_6^{2-}$ only.

The analytical procedure is summarized as follows:

An appropriate aliquot of sample (the aliquot size depends on the range of polythionate concentration - a 25 ml aliquot, by trial and error, proved sufficient) is pipetted into a beaker, to which is added 3 ml of formaldehyde, if the sulphite anion concentration exceeds 40 mg/l. The sample is then titrated to an end point of pH 8.2

with either 0.005 N or 0.01 N caustic solution taking care to avoid excessive dilution. The pH electrode is removed and rinsed with distilled water into the sample. Then, 5 ml of a 2% (w/v) mercuric chloride solution is added to the sample. The sample is then diluted to a final volume of 60 ± 10 ml and allowed to stand at room temperature for about 5 minutes. It is then heated and brought rapidly to a boil, after which it is allowed to cool to room temperature. After cooling to room temperature, a 20% (w/v) potassium iodide solution is added until the resulting orange precipitate that develops just disappears. (Avoid excessive addition of potassium iodide.) The sample is then titrated with a standardized 0.005 N sodium hydroxide solution to the initial end point pH 8.2.

The concentration of polythionate is expressed as (mg/l) thiosulphate and is given by

$$\text{mg/l as } S_2O_3^{2-} = \frac{(T+V)N}{A} (56{,}000)$$

where T = ml of 0.005 NaOH added to get back to initial end point of pH 8.2

N = normality of caustic solution

A = ml of sample

V = equivalent amount of base in ml for a distilled water blank

(V = 0.67)

4.3.4 Sulphate

The method used was from a report by F. Standeven (27) of the University of Waterloo, Waterloo, Ontario, and consists of titration of the sample with barium perchlorate in an alcoholic medium under controlled acid conditions. Thorin is used as the indicator. Cations, sulphite, thiosulphate and phosphate interfere with the analysis, however, cations are removed by an ion exchange column (Na^+ based), sulphite was never detected during the study, and the low effluent thiosulphate concentration was considered to be negligible. Phosphate was removed by the addition of excess magnesium carbonate, which precipitated the phosphate as magnesium phosphate.

The method is valid for sulphate concentrations up to 500 mg/l, but by sample dilution larger concentrations can be brought to within this range. The error is given as ±10%.

This procedure for sulphate analysis was chosen over those in Standard Methods on the recommendation of Dr. Brian LeClair, Department of the Environment, Place Vincent Massey, Hull.

The analytical procedure is summarized as follows:

Phosphate is first removed from the sample by precipitation with magnesium carbonate. The addition of excess magnesium carbonate serves as a carrier to ensure complete precipitation of the phosphate, and the removal of phosphate is essentially complete if the precipitate is filtered cold.

The sample is then passed through an ion exchange column 10 to 15 mls at a time, discarding the effluent. This process is repeated three times. An appropriate aliquot of the next effluent sample of up to 10 mls and containing at least 50 μg SO_4^{2-} is pipetted into a small white porcelain dish. (The aliquot is diluted, if necessary, to 10 mls with distilled water.) Then, 40 mls of alcohol (2-propanol) are added and also two drops of a 0.2% (w/v) Thorin indicator solution. The sample pH is then adjusted, using a pH meter and electrode, to between pH 2.5 and 4.0, with either dilute NH_4OH or dilute HCl. The sample is then titrated with 0.005 m barium perchlorate ($Ba(ClO_4)_2$) until it just turns pink.

In the event that the SO_4^{2-} concentration exceeds the analytical range of the test, the sample can be diluted to bring it within the range. For this study, a (1:10) dilution was used as the effluent SO_4^{2-} concentration exceeded the range of the analysis.

The calculation is given by:

$$\text{mg/l } SO_4^{2-} = (SO_4 \text{ FACTOR})(\text{Sample titration} - \text{Reagent Blank Titration})$$

where the (SO_4 FACTOR) is obtained from several standard sulphate solutions ranging from 10 to 100 mg/l. A factor was determined for each standard sulphate solution as

$$\text{factor} = \left[\frac{\text{Standard sulphate solution (mg/l)}}{\left(\begin{array}{c}\text{Titration for}\\ \text{standard sulphate solution}\end{array}\right) - \left(\begin{array}{c}\text{Titration for}\\ \text{Reagent Blank}\end{array}\right)}\right]$$

The (SO_4 FACTOR) used in the calculation above, was the average of all factors for each standard solution.

4.3.5 Mixed Liquor Total Suspended Solids and Mixed Liquor Volatile Suspended Solids

The procedure followed was from Millipore Filters.

A sample is passed over a pre-washed, dried and weighed Whatman 4.25 cm glass fiber filter. The filter and residue are then dried at 110°C for one hour, dessicated and weighed. Gain in weight is interpreted as MLTSS.

The filter and residue is then placed in an oven at 550°C - 600°C for 30 minutes, dessicated and weighed. Loss in weight is interpreted as MLVSS.

Weighings were performed on a Mettler H101T balance accurate to four significant figures.

A measure of the precision of the MLTSS and MLVSS analyses were not available from the Millipore literature, thus an accurate statement in this regard cannot be given. However, Standard Methods (1) reports a similar procedure for suspended solids as giving a standard deviation of ±5.2 mg/l at 15 mg/l; ±24 mg/l at 242 mg/l, and ±13 mg/l at 1707 mg/l.

4.3.6 pH

pH is a measure of the hydrogen ion activity and was determined with a Fisher Accumet pH meter, Model 210, employing a glass electrode. The meter was calibrated daily with a standard buffer solution of pH 4.01 at 25°C.

The accuracy is given as ±0.1 pH unit.

4.3.7 Turbidity

Turbidity, for a thiosulphate oxidizing system, is indicative of both bacteria and elemental sulphur, produced by a thiosulphate oxidation and was measured with a Turbidity meter, Model DRT 100, made by HF Instruments, Bolton, Ontario.

Before use, however, the instrument must be calibrated with a standard solution of 0.13 Nelphometric Turbidity Units (NTU).

The turbidity of the sample is read directly from the dial in NTU, using the appropriate scale.

The resolution and linearity of the turbidity meter was stated by the manufacturer as ±1% of full scale.

4.3.8 Temperature

The bacteria responsible for thiosulphate oxidation are temperature sensitive, thus a daily temperature of the laboratory and mixed liquor was taken with a conventional mercury thermometer, from Fisher Scientific, having a range from -20°C to +110°C, with an accuracy of ±0.5°C.

CHAPTER 5

RESULTS

5.1 Influent Phosphorous Variation Study

The phosphorous variation study was an attempt to determine the effect different influent phosphorous concentrations (phosphorous supplied as KH_2PO_4) would have on the biological oxidation of thiosulphate.

Experiments were conducted, at room temperature, in continuous flow completely mixed reactors without recycle. Three reactors were used, each supplied with phosphorous concentrations different from each other and greater than the minimum required amount, as determined from bacterial growth kinetics.

Reactor (1) received an influent phosphorous concentration greater than the minimum amount by a factor of 2.2, Reactor (2) an amount greater by a factor of 7.1, and Reactor (3) an amount greater by a factor of 12.0.

The study was conducted for a duration of twenty days, until the obvious failure of Reactor (3) ended experimentation. Reactor (1) and Reactor (2), however, were still functioning efficiently after this time, and were considered to be operating under steady-state conditions.

Table 18 summarizes the ambient room temperature and Reactor Mixed Liquor Temperature (MLT) for the duration of the study. The highest room temperature recorded was 27°C, and the lowest 23°C.

TABLE 18 AMBIENT ROOM TEMPERATURE AND MIXED LIQUOR TEMPERATURE OF REACTORS 1, 2, 3 - PHOSPHOROUS VARIAT
STUDY

		REACTOR 1	REACTOR 2	REACTOR 3
DAY	ART* (°C)	Mixed Liquor Temperature (°C)	Mixed Liquor Temperature (°C)	Mixed Liquor Temperature (°C)
1	23	22	23	23
2	25	23	23	24
3	24	22	23	23
4	25	22	23.5	24
5	24.5	23	23	24
6	25	23	23.5	24
7	25	23	24	24
8	24	23	23.5	24
9	24.5	23	24	24
10	24	22.5	23.5	23.5
11	25.5	23.5	24.5	25
12	25.5	23.5	24.5	25
13	26	24	24.5	24.5
14	25.5	24	24.5	25
15	25	24	24	24.5
16	25.5	24	24.5	24.5
17	26	24	24.5	24.5
18	26.5	25	25.5	25.5
19	26.5	25.5	25.5	25.5
20	27	25	26	25.5

* ART - Ambient Room Temperature

Reactor MLT followed the room temperature variation with Reactor (1) exhibiting a MLT consistently lower than Reactor (2) and Reactor (3), by amounts varying from 1/2°C to 1°C. Reactor (2) had a MLT more or less the same as Reactor (3), with any difference between them being no greater than 1/2°C.

The consistently lower temperatures of Reactor (1) was most probably due to its location, situated, as it was, adjacent to a window for the duration of the study, which was conducted during February and March.

Table 19 presents the influent, mixed liquor and effluent pH values for Reactors (1), (2) and (3).

For Reactor (1), the influent pH was consistently above pH 7.00, with the highest and lowest values being pH 7.45 and pH 7.00, respectively.

For Reactor (2), the influent pH values were consistently lower than those of Reactor (1), greater than those of Reactor (3) and varied around the pH 7.00 value. The highest and lowest values were pH 7.20 and pH 6.90, respectively.

For Reactor (3), the influent pH values were always less than those of Reactor (1) and Reactor (2), except on day one, and was greater than or equal to pH 7.0 on only three occasions. The highest and lowest values were pH 7.15 and pH 6.80, respectively.

For Reactors (1), (2) and (3), both mixed liquor and effluent pH values were, after day four and up to day fourteen, constant at pH

TABLE 19 INFLUENT, MIXED LIQUOR AND EFFLUENT pH FOR REACTORS 1,2,3 - PHOSPHOROUS VARIATION STUDY

DAY	REACTOR 1			REACTOR 2			REACTOR 3		
	Influent pH	Mixed Liquor pH	Effluent pH	Influent pH	Mixed Liquor pH	Effluent pH	Influent pH	Mixed Liquor pH	Effluent pH
1	7.10	2.20	2.20	7.10	2.10	2.20	7.15	2.20	2.20
2	7.10	2.15	2.15	7.00	2.15	2.15	6.95	2.20	2.20
3	7.30	2.10	2.10	7.10	2.10	2.10	6.90	2.10	2.10
4	7.30	2.15	2.15	7.10	2.10	2.10	6.90	2.10	2.10
5	7.20	2.10	2.10	7.00	2.10	2.10	6.85	2.10	2.10
6	7.20	2.10	2.10	7.00	2.05	2.10	6.90	2.10	2.10
7	7.30	2.10	2.10	7.00	2.10	2.10	6.85	2.10	2.10
8	7.30	2.15	2.15	7.05	2.10	2.10	6.85	2.10	2.10
9	7.30	2.15	2.15	7.00	2.10	2.10	6.85	2.10	2.10
10	7.30	2.10	2.10	7.00	2.10	2.10	6.90	2.10	2.10
11	7.25	2.10	2.10	6.95	2.10	2.10	6.80	2.10	2.10
12	7.45	2.10	2.10	7.25	2.10	2.10	7.05	2.10	2.10
13	7.25	2.10	2.10	7.00	2.10	2.10	6.90	2.10	2.10
14	7.40	2.10	2.10	7.20	2.10	2.10	7.00	2.10	2.10
15	7.10	2.10	2.10	6.90	2.10	2.10	6.90	2.25	2.25
16	7.30	2.10	2.10	7.10	2.10	2.10	6.90	2.35	2.35
17	7.30	2.10	2.10	7.10	2.10	2.10	6.90	2.45	2.45
18	7.20	2.10	2.10	6.90	2.10	2.10	6.80	2.55	2.55
19	7.20	2.10	2.10	6.90	2.10	2.10	6.90	2.75	2.75
20	7.00	2.10	2.10	6.90	2.10	2.10	6.70	2.85	2.85

2.10. This equality of mixed liquor and effluent pH values is attributed to a complete mix without recycle regime, whereby, due to the absence of recycle, reactor mixed liquor and effluent are similar, if not identical.

Table 20 summarizes values of the Mixed Liquor Total Suspended Solids (MLTSS) and Mixed Liquor Volatile Suspended Solids (MLVSS) for Reactors (1), (2) and (3).

These values are inconsistent in that on some occasions, MLVSS exceeded MLTSS, and each reactor had occasions when this occurred - Reactor (1) on two occasions, Reactor (2) on three occasions, and Reactor (3) on eight occasions.

The highest and lowest MLTSS values were: 76 mg/l and 4 mg/l, respectively, for Reactor (1); 68 mg/l and 0 mg/l, respectively, for Reactor (2); 28 mg/l and 0 mg/l, respectively, for Reactor (3). Highest and lowest MLVSS values were: 28 mg/l and 2 mg/l, respectively for Reactor (1); 28 mg/l and 0 mg/l, respectively, for Reactor (2); 28 mg/l and 2 mg/l, respectively, for Reactor (3).

During the Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS) analyses, a 25 ml sample of Reactor Mixed Liquor was used, and due to the low solids and bacterial concentration, this insufficient sample volume is thought to account for the inconsistent results. As an additional check, 50 ml samples of effluent were also simultaneously analyzed for TSS and VSS. Also, as the system used was one of complete mix without recycle, it was assumed these values would be compatible. Results, however, from using 50 ml effluent samples

TABLE 20 MLTSS AND MLVSS FOR REACTORS 1,2,3 - PHOSPHOROUS VARIATION STUDY

DAY	REACTOR 1		REACTOR 2		REACTOR 3	
	MLTSS* (mg/1)	MLVSS** (mg/1)	MLTSS (mg/1)	MLVSS (mg/1)	MLTSS (mg/1)	MLVSS (mg/1)
1	36	28	36	28	28	28
2	16	12	8+	--	4+	--
3	76	28	68	28	20+	--
4	16	12	28	24	8+	--
5	24	12	16	16	24	16
6	12	12	16	12	16+	--
7	20	16	24	24	16	8
8	12	12	8	8	16+	--
9	20	16	16	12	16	12
10	16+	--	12+	--	4+	--
11	20	20	28	0	12	4
12	24	20	16	12	12	8
13	12	10	8	8	8	8
14	10	10	6	6	12	10
15	16	16	8	8	8	8
16	8	8	8	6	8	6
17	8	4	12	8	4	2
18	4	4	26	18	2	2
19	4	4	8	4	0+	--
20	4	2	0+	--	0+	--

* MLTSS - Mixed Liquor Total Suspended Solids ** MLVSS - Mixed Liquor Volatile Suspended Solids
+ MLTSS < MLVSS Precision of test resulted in these anomalies.

were as inconsistent as the 25 ml mixed liquor samples, and, therefore, are not included in this report. Table 21 presents values of the effluent turbidity in Nelphometric Turbidity Units (NTU), for Reactors (1), (2) and (3). On two occasions, day one and day nineteen, results were not obtained due to instrument trouble.

The results are inconstant and could be due to either the inconstant MLTSS and MLVSS values, or an insufficient warm-up time for the instrument, although the stipulated one hour warm-up was used.

The highest effluent turbidity readings for Reactors (1) and (2) are on day two, and prior to its failure on day fourteen, the highest effluent turbidity for Reactor (3) was also on day two. This high initial turbidity of each reactor is thought to be due to the adjustment of the reactors from batch operation to continuous flow operation. Batch operations were used for acclimatization purposes prior to the start of continuous flow operations.

Table 22 documents the influent and effluent COD and percent COD removal for Reactors (1), (2) and (3).

A comparison of influent COD values for each reactor, shows that these values were similar and consistently above 500 mg/1, except on one occasion for each reactor when it was below 500 mg/1.

A comparison of effluent COD values for Reactors (1), (2) and (3) shows that during day one and two, Reactor (1) had a lower effluent COD than either Reactor (2) or Reactor (3), but that by day three all reactors showed similar effluent COD and percent COD removal values.

TABLE 21 EFFLUENT TURBIDITY OF REACTORS 1, 2, 3 - PHOSPHOROUS VARIATION STUDY

	REACTOR 1	REACTOR 2	REACTOR 3
DAY	Effluent Turbidity (NTU)*	Effluent Turbidity (NTU)*	Effluent Turbidity (NTU)*
1	--	--	--
2	16	25	23
3	12.5	11	11
4	6.5	8	14
5	9	12	15
6	14	11	16
7	12	19	14
8	13	17	14
9	8	12	11
10	12	12	10
11	9	10	10
12	10	14	9
13	12	12	10
14	7	13	1000
15	7	14	100
16	10	10	28
17	10	10	20
18	8	9	18
19	--	--	--
20	9	12	6

*NTU - Nelphometric Turbidity Units

TABLE 22 INFLUENT AND EFFLUENT COD AND PERCENT COD REMOVAL FOR REACTORS 1,2,3 - PHOSPHOROUS VARIATION STUDY

DAY	REACTOR 1			REACTOR 2			REACTOR 3		
	Influent COD* (mg/l)	Effluent COD (mg/l)	Removal COD (%)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (%)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (%)
1	507.0	42.5	91.6	514.0	58.5	88.6	526.0	81.5	84.5
2	494.0	27.0	94.58	496.0	53.0	89.29	501.5	41.0	91.58
3	519.0	28.0	94.5	526.0	25.0	95.3	524.5	23.0	95.6
4	517.0	27.0	94.8	524.5	23.0	95.6	526.0	25.0	95.3
5	528.0	32.0	93.9	528.0	34.0	93.6	496.0	32.0	93.6
6	519.0	44.0	91.5	526.0	44.0	91.6	530.0	35.0	93.3
7	514.0	38.0	92.6	525.0	40.0	92.4	524.0	30.0	94.2
8	528.0	37.0	92.6	521.0	41.0	92.18	521.0	35.0	93.2
9	514.0	31.5	93.87	518.0	37.0	92.78	518.0	31.5	93.9
10	516.0	35.0	93.13	512.0	35.0	93.10	521.5	26.5	95.1
11	520.0	29.5	94.3	518.0	35.0	93.16	520.0	28.0	94.7
12	518.0	24.0	95.44	520.0	33.5	93.56	521.5	20.0	96.23
13	525.5	31.50	94.0	529.0	39.0	92.56	521.5	31.5	93.96
14	529.0	26.0	95.16	521.5	41.0	92.10	541.0	29.5	94.55
15	525.5	24.0	95.5	525.5	35.0	93.26	525.5	22.0	95.88
16	525.5	24.0	95.5	525.5	35.0	93.26	529.0	108.0	79.55
17	523.5	28.0	94.7	520.0	35.0	93.18	535.0	160.0	70.18
18	511.0	26.0	94.85	525.0	28.0	94.70	517.0	169.0	67.27
19	508.0	34.0	93.33	523.0	34.0	93.5	523.0	209.0	60.07
20	513.0	34.0	93.4	517.0	36.0	93.10	519.0	224.0	56.89

* COD - Chemical Oxygen Demand

When the reactors were operating efficiently, effluent COD remained below 45 mg/1 and COD removal was better than 91 percent.

Figures 7,8 and 9 illustrate graphically the variation of influent and effluent COD for Reactors (1), (2) and (3), and Figure 10 compares the effluent COD of the reactors.

The lower COD removal during day one and two, experienced by all reactors, is thought to be due to the adjustment from batch operation to continuous flow operation.

Reactor (3) operated efficiently up to day fifteen, when the effluent COD was 22.0 mg/1 and COD removal was 95.88 percent. On day sixteen, effluent COD was 108.0 mg/1, effluent pH 2.25, MLTSS and MLVSS were 8 mg/1 and 8 mg/1, respectively, and COD removal was 79.5 percent, a decrease from day fifteen. From this point on, effluent COD increased and percent COD removal decreased to 224.0 mg/1 and 56.9 percent, respectively, by day twenty. On day twenty, Reactors (1) and (2) showed, respectively, 93.4 and 93.1 percent COD removals and were considered to be functioning efficiently.

Table 23 lists the influent and effluent thiosulphate concentrations for Reactors (1), (2) and (3). In practice, 2000 mg of $Na_2S_2O_3.5H_2O$ were added per litre of influent, resulting in a theoretical $S_2O_3^{2-}$ concentration of 904 mg/1. Influent $S_2O_3^{2-}$ concentrations were not, however, near this value for either of Reactors (1), (2) or (3).

Highest and lowest influent $S_2O_3^{2-}$ concentrations were 729.0 mg/1 and 688.0 mg/1, respectively, for Reactor (1); 706.0 mg/1 and 681.0 mg/1, respectively, for Reactor (2), and 709.0 mg/1 and 683.0 mg/1

Figure (7). Influent and Effluent COD values for Reactor (1)

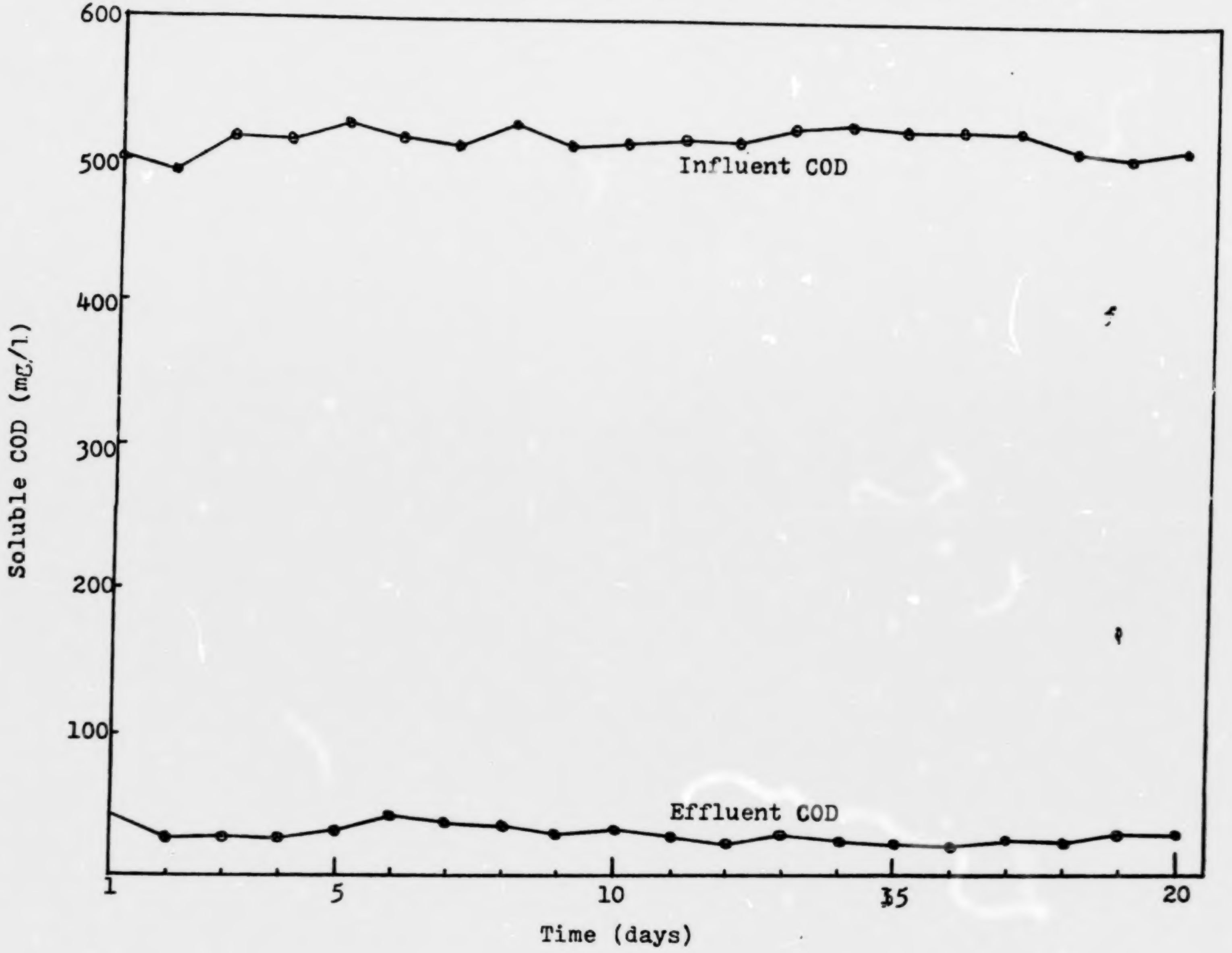


Figure (8). Influent and Effluent COD values for Reactor (2)

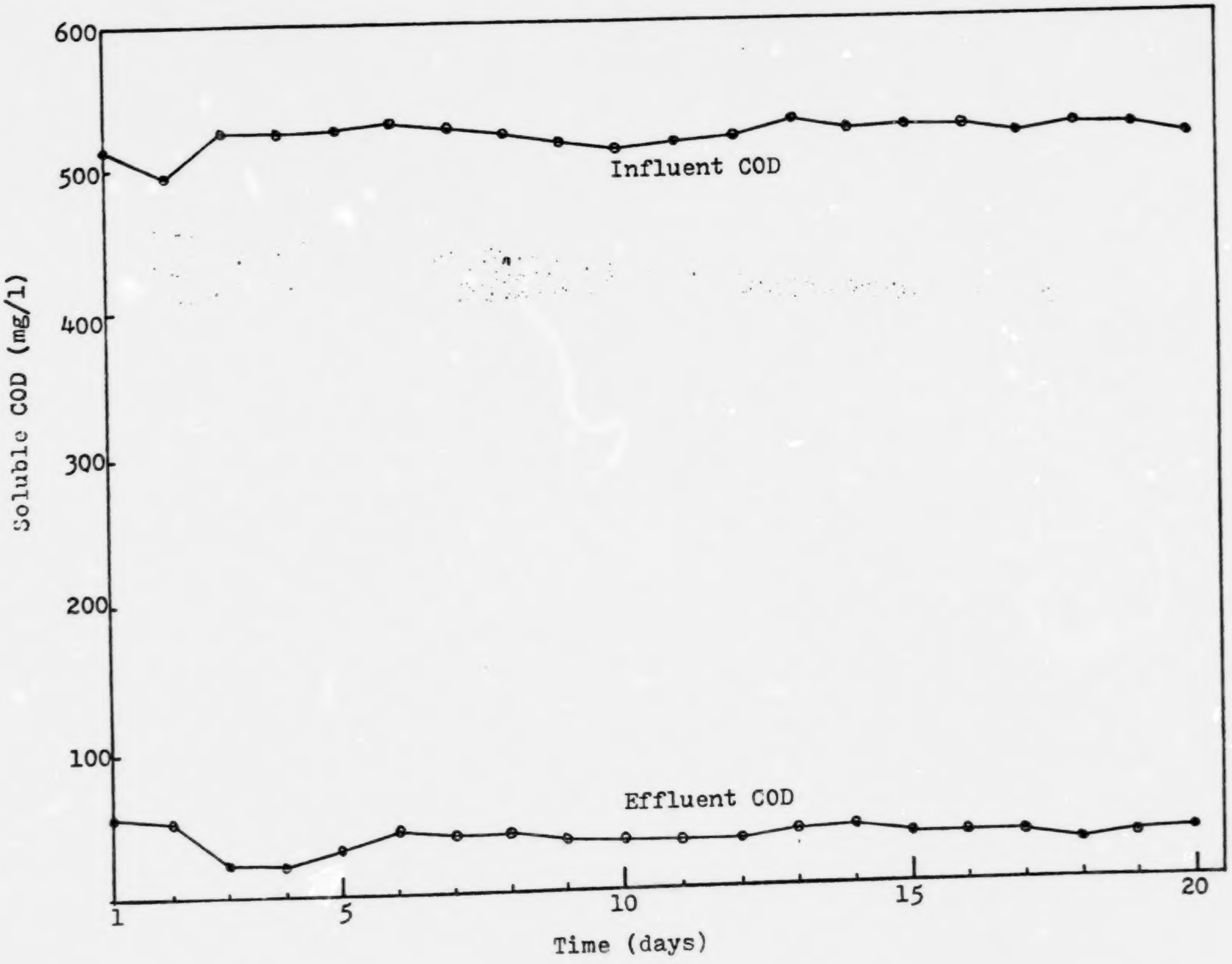


Figure (9). Influent and Effluent COD values for Reactor (3)

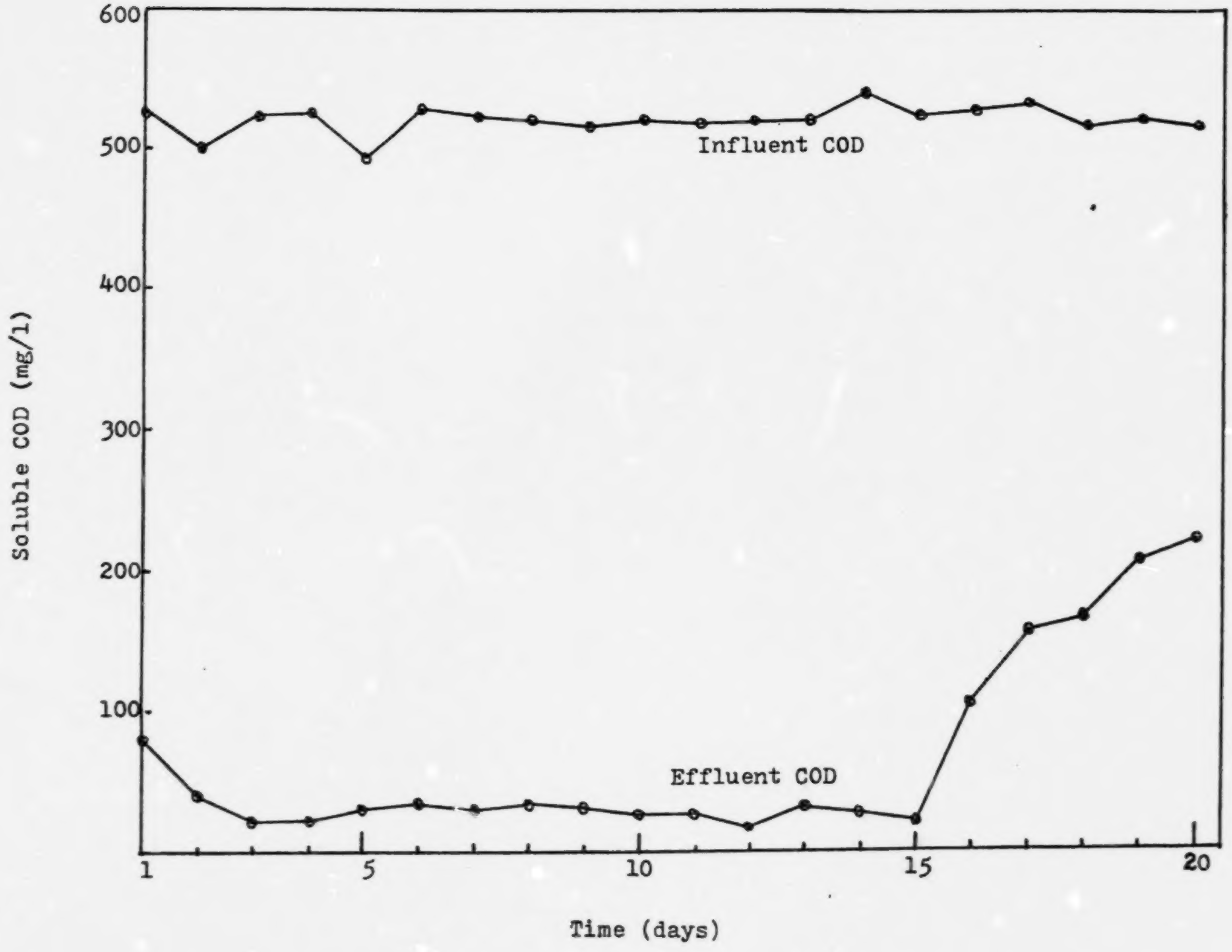


Figure (10). A Comparison of Effluent COD values for Reactors 1, 2, 3.

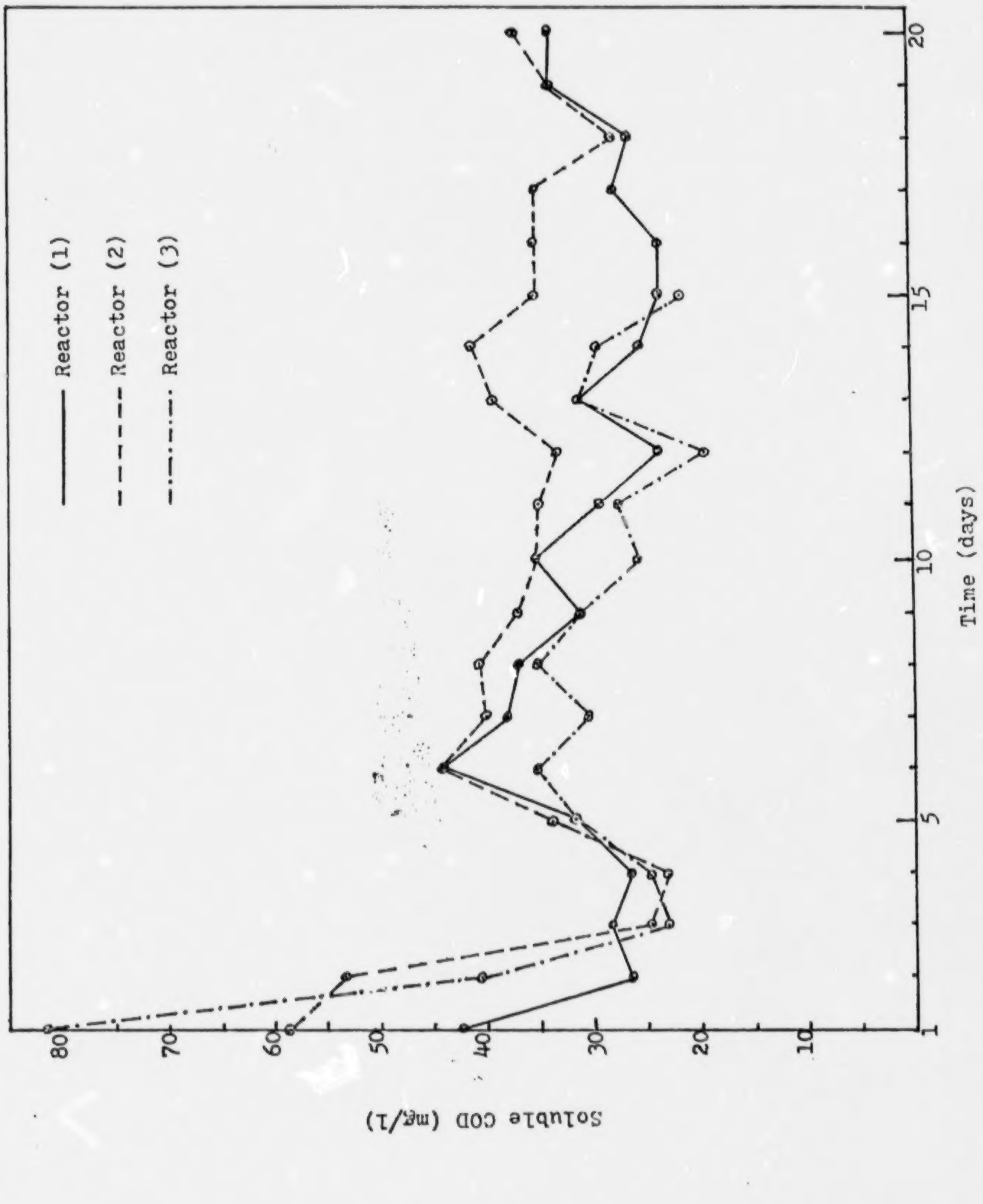


TABLE 23 INFLUENT AND EFFLUENT S_2O_3 FOR REACTORS 1,2,3 - PHOSPHOROUS VARIATION STUDY

	REACTOR 1		REACTOR 2		REACTOR 3	
DAY	Influent $S_2O_3^{2-}$ (mg/l)	Effluent $S_2O_3^{2-}$ (mg/l)	Influent $S_2O_3^{2-}$ (mg/l)	Effluent $S_2O_3^{2-}$ (mg/l)	Influent $S_2O_3^{2-}$ (mg/l)	Effluent $S_2O_3^{2-}$ (mg/l)
1	706.0	3.0	706.0	3.0	709.0	3.5
2	729.0	3.5	706.0	3.5	694.0	3.5
3	694.0	1.5	694.0	3.0	692.0	3.0
4	694.0	3.0	694.0	3.0	692.0	3.0
5	694.0	3.0	692.0	3.0	687.0	3.0
6	692.0	3.0	692.0	3.0	692.0	3.0
7	688.0	3.0	685.0	3.0	690.0	3.0
8	690.0	3.0	681.0	3.0	690.0	3.0
9	692.0	3.0	690.0	3.0	692.0	3.0
10	694.0	3.0	674.0	3.0	704.0	3.0
11	688.0	3.0	685.0	3.0	683.0	3.0
12	692.0	3.0	690.0	3.0	692.0	3.0
13	690.0	3.0	688.0	3.0	697.0	3.0
14	692.0	3.0	694.0	3.0	692.0	3.0
15	688.0	3.0	683.0	3.0	690.0	3.0
16	692.0	3.0	681.0	3.0	692.0	3.0
17	692.0	3.0	683.0	3.0	697.0	3.0
18	694.0	3.0	683.0	3.0	702.0	3.0
19	692.0	3.0	685.0	3.0	695.0	3.5
20	690.0	3.0	692.0	3.0	695.0	4.0

respectively, for Reactor (3). The difference between highest and lowest influent $S_2O_3^{2-}$ concentrations can be attributed to errors in weighing. However, the signifiant departure from the theoretical value cannot be accounted for apart from analytical errors and possible oxidation of thiosulphate during storage in the influent bottle.

Effluent $S_2O_3^{2-}$ concentration was, for all reactors, 3.0 mg/l after day three, and after the adjustment from batch to continuous flow had been made by the reactors. These effluent $S_2O_3^{2-}$ concentrations were constant for Reactors (1) and (2) throughout the duration of the study. However, for Reactor (3) effluent $S_2O_3^{2-}$ increased to 3.5 mg/l on day nineteen and was 4.0 mg/l on day twenty.

It is noteworthy that, although Reactor (3) started to fail on day sixteen of the parameters, only effluent $S_2O_3^{2-}$ remained constant after day sixteen and showed change only on day nineteen. Other parameters such as effluent COD, effluent pH, effluent polythionates and effluent sulphate, immediately reflected the incipient failure of Reactor (3) on day sixteen.

Table 24 summarizes the effluent polythionate concentrations, expressed as mg/l $S_2O_3^{2-}$, for Reactors (1), (2) and (3). Polythionates measured by the analytical procedure used were: $S_3O_6^{2-}$ (trithionate), $S_4O_6^{2-}$ (tetrathionate) and $S_5O_6^{2-}$ (pentathionate). Influent polythionate concentration was assumed to be zero mg/l at all times. This assumption was never checked.

Highest and lowest effluent polythionate concentrations were 59.0 mg/l and 19.0 mg/l, respectively, for Reactor (1), 93.0 mg/l and

28.0 mg/l, respectively, for Reactor (2) and, prior to day fifteen, 80.0 mg/l and 34.0 mg/l, respectively, for Reactor (3).

Effluent polythionate concentration for each reactor followed a definite trend, as can be seen from Table 24 and Figure 11 , a graphical representation of effluent polythionate. All reactors exhibited periods of simultaneous rising and falling together. From day two to day four, Reactor (1) showed the greatest effluent polythionate concentration, with Reactors (2) and (3) interchanging positions as to second greatest polythionate concentration. From day five to day twenty, Reactor (1) exhibited the least effluent polythionate concentration, with Reactors (2) and (3) interchanging positions of greatest effluent polythionate production. From day eight to day fourteen, however, effluent polythionate concentration for Reactor (3) was consistently greater than Reactor (2).

For Reactors (1) and (2) there are somewhat linear portions in Figure 11 from day nine to day twenty, with exceptions at day fourteen and day nineteen, for Reactor (1), and day fifteen and day twenty, for Reactor (2).

The onset of failure for Reactor (3), on day sixteen, can be observed by the marked increase in effluent polythionate concentration over day fifteen.

The initial high values of effluent polythionate on day one, for each reactor, is attributed to the adjustment from batch to continuous flow operation.

TABLE 24 EFFLUENT POLYTHIONATE AS $S_2O_3^{2-}$ FOR REACTORS 1, 2, 3 - PHOSPHORCUS VARIATION STUDY

DAY	REACTOR 1 Effluent Polythionate (mg/l) as $S_2O_3^{2-}$	REACTOR 2 Effluent Polythionate (mg/l) as $S_2O_3^{2-}$	REACTOR 3 Effluent Polythionate (mg/l) as $S_2O_3^{2-}$
1	51.0	93.0	80.0
2	59.0	37.0	46.0
3	62.0	57.0	52.0
4	44.0	41.0	34.0
5	22.0	28.0	37.0
6	26.0	43.0	41.0
7	61.0	78.0	61.0
8	43.0	62.0	71.0
9	30.0	38.0	41.0
10	36.0	46.0	46.0
11	30.0	41.0	54.0
12	27.0	43.0	48.0
13	22.0	46.0	44.0
14	37.0	42.0	47.0
15	22.0	33.0	56.0
16	23.0	42.0	235.0
17	22.0	42.0	299.0
18	26.0	48.0	341.0
19	35.0	46.0	375.0
20	19.0	34.0	404.0

Figure (11). A Comparison of Effluent Polythionate Concentrations for Reactors 1, 2, 3.

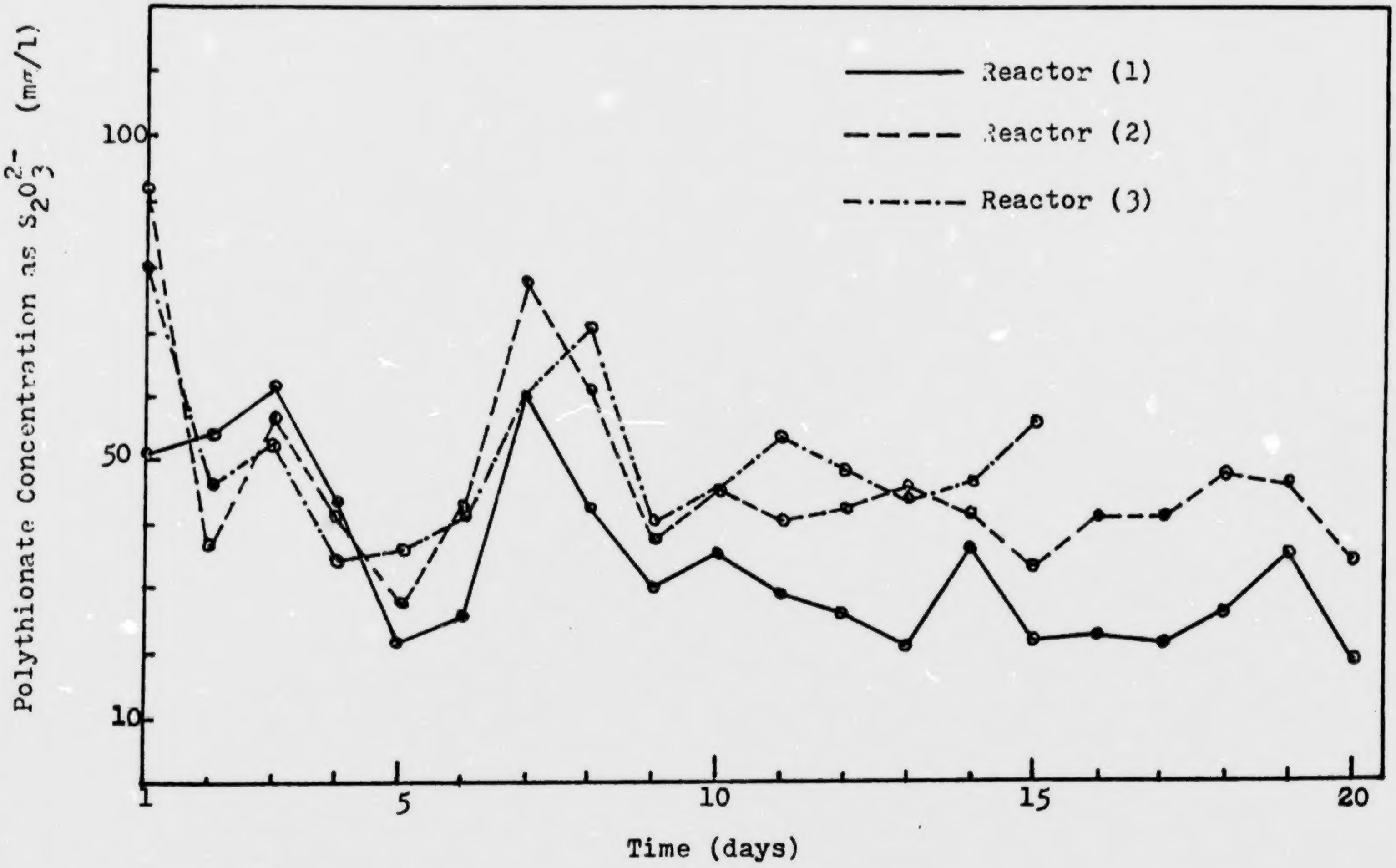


Table 25 presents the influent and effluent sulphate concentrations for Reactors (1), (2) and (3).

As can be observed, the influent sulphate concentration for each reactor was constant at 60 mg/l, for the duration of the study. Sources of influent sulphate were the trace element solution and tap-water. This constancy of influent sulphate is thought to be due to the sensitivity of the analytical procedure as well as the manner in which the influent sample was obtained for analysis. (The sample for the determination of influent sulphate was obtained by taking 20 ml of trace elements solution, diluting to 2 ℓ with tap water and taking appropriate aliquots with which to perform the analysis. The constancy of the influent sulphate concentration is considered to be due to the constant strength of the trace elements solution).

Highest and lowest effluent sulphate concentrations were 1724 mg/l and 1333 mg/l, respectively, for Reactor (1), 1749 mg/l and 1406 mg/l, respectively, for Reactor (2) and prior to day sixteen, 1775 mg/l and 1168 mg/l, respectively, for Reactor (3).

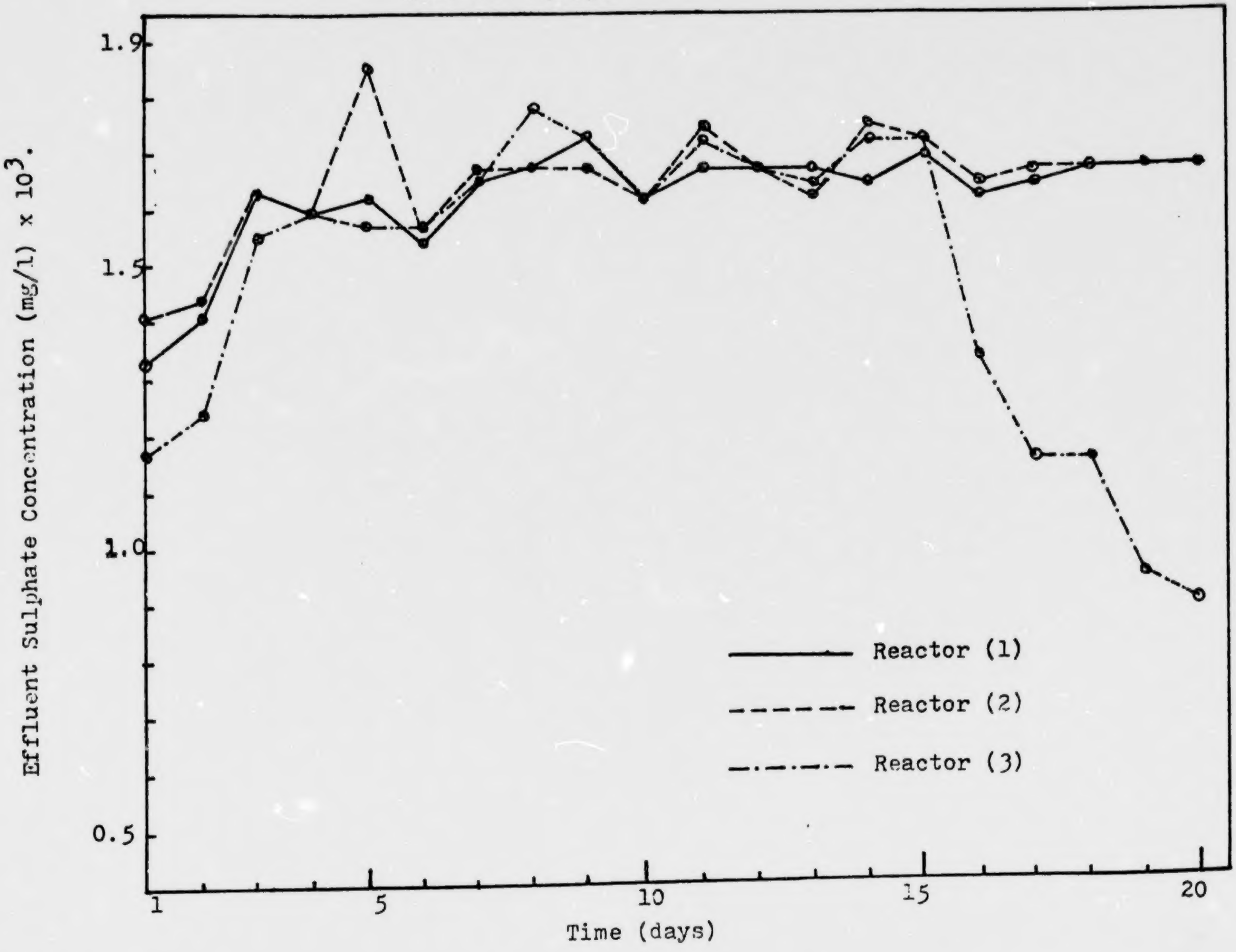
Figure 12 shows the effluent sulphate concentration for Reactors (1), (2) and (3). Notable features are the low initial effluent sulphate concentrations, for each reactor, on day one. This is thought to be due to the adjustment of the reactors from batch to continuous flow operation. After day six, however, effluent sulphate values are reasonably similar for all reactors.

The failure of Reactor (3), after day fifteen, is observed in Figure 6 as a decreasing effluent sulphate concentration.

TABLE 25 INFLUENT AND EFFLUENT SO_4 FOR REACTORS 1,2, 3 - PHOSPHOROUS VARIATION STUDY

	REACTOR 1		REACTOR 2		REACTOR 3	
DAY	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)
1	60	1333	60	1406	60	1168
2	60	1401	60	1437	60	1240
3	60	1633	60	1633	60	1550
4	60	1594	60	1594	60	1594
5	60	1620	60	1853	60	1569
6	60	1543	60	1569	60	1569
7	60	1646	60	1672	60	1646
8	60	1672	60	1672	60	1775
9	60	1724	60	1672	60	1724
10	60	1620	60	1620	60	1620
11	60	1672	60	1749	60	1724
12	60	1672	60	1672	60	1672
13	60	1672	60	1620	60	1646
14	60	1646	60	1749	60	1724
15	60	1698	60	1724	60	1724
16	60	1620	60	1646	60	1336
17	60	1646	60	1672	60	1155
18	60	1672	60	1672	60	1155
19	60	1672	60	1672	60	948
20	60	1672	60	1672	60	896

Figure (12). A Comparison of Effluent Sulphate Concentrations for Reactors 1,2,3.



5.2 Retention Time Variation Study

The retention time variation study was an attempt to determine the minimum retention time capable of facilitating the biological oxidation of thiosulphate. During this study, influent characteristics remained constant as to thiosulphate, nutrient (N,P) and trace element concentrations. By varying the influent flowrate, retention time could be changed.

Experiments were conducted at room temperature in continuous flow completely mixed reactors without recycle until either steady-state conditions were reached or failure (i.e., washout), at a particular value of retention time, occurred. If steady-state conditions prevailed at a particular value of retention time, experiments were conducted for ten days, whereupon the retention time was changed to a new, lower, value.

Due to the limited number of reactors and the daily time constraints for analysis, not all of the retention time studies could be performed simultaneously. The chronological proceedings of this study was, therefore, divided into two parts, as shown below:

TABLE 26

Chronology of Retention Time Study

		Reactor Number		
		1	2	3
First Study	Retention time (days)	4	3	2
Second Study	Retention time (days)	1/2	1	1/4

Thus, when experiments with Reactor (1), operating at 4 days retention time, were completed the retention time was changed to 1/2 day. Similarly for Reactor (2), from a retention time of 3 days to 1 day and for Reactor (3) from a retention time of 2 days to 1/4 day.

Results with retention time at 1/4 day are not included as reactor failure at this retention time was immediate.

Table 27 summarizes the ambient room temperature and reactor mixed liquor temperature for each value of retention time.

Reactor mixed liquor temperatures were fairly consistent with the greatest temperature difference between maximum and minimum being no greater than 1.5°C. This value, possibly, to the fact that the study was conducted during March and April, when the laboratory maintained more consistent temperatures.

Table 28 presents the influent, mixed liquor and effluent pH values during the retention time variation study.

Influent pH values are no lower than pH 6.75 and no greater than pH 7.40, a value recorded during the 2 day retention time study.

Mixed liquor and effluent pH values were constant for retention time values from 4 days to 1 day, at pH 2.1. For the 1/2 day retention time study, the mixed liquor and effluent pH was 2.55 on day one, but by day two, was pH 2.1. This initial increase to pH 2.55 on day one is attributed to a "shock effect" resulting in the change of retention time from the previous value of 4 days, the proceeding retention time study, to 1/2 day.

TABLE 27 AMBIENT ROOM TEMPERATURE AND MIXED LIQUOR TEMPERATURE DURING θc VARIATION STUDY

		θc = 4 DAYS	θc = 3 DAYS		θc = 2 DAYS		θc = 1 DAY		θc = ½ DAY
DAY	ART*	Mixed Liquor Temp	Mixed Liquor Temp	ART*	Mixed Liquor Temp	ART*	Mixed Liquor Temp	ART*	Mixed Liquor Temp
1	26.0°C	25.0°C	25.0°C	24.0°C	24.0°C	25°C	24.5°C	25°C	24.5°C
2	25.5	24.5	25.0	24.0	24.0	25	25.0	23.5	23.0
3	25.0	24.0	25.0	25.0	24.5	23.5	23.0	24.0	23.5
4	25.0	24.0	24.5	24.5	24.0	24.0	23.5	24.0	24.0
5	24.0	23.5	24.0	24.5	24.0	24.0	24.0	24.0	23.5
6	24.0	23.5	24.0	24.0	24.0	24.0	24.0	23.5	23.0
7	25.0	24.0	24.5	24.5	24.0	23.5	23.0	23.5	23.0
8	24.5	24.0	24.5	25.0	24.5	23.5	23.5	24.0	23.0
9	24.5	24.0	24.5	25.0	25.0	24.0	23.5	25.0	24.0
10	24.0	23.5	24.0	25.0	25.0	25.0	24.5	25.0	24.5

* ART - AMBIENT ROOM TEMPERATURE

TABLE 28 INFLUENT, MIXED LIQUOR AND EFFLUENT pH FOR θc VARIATION STUDY

DAY	θc = 4 DAYS			θc = 3 DAYS			θc = 2 DAYS			θc = 1 DAY			θc = : DAY		
	Influent pH	ML* pH	Effluent pH	Influent pH	ML pH	Effluent pH	Influent pH	ML pH	Effluent pH	Influent pH	ML pH	Effluent pH	Influent pH	ML pH	Effluent pH
1	6.75	2.10	2.10	6.80	2.10	2.10	7.10	2.10	2.10	7.00	2.10	2.10	7.10	2.55	2.55
2	6.75	2.10	2.10	6.85	2.10	2.10	7.30	2.10	2.10	7.15	2.10	2.10	7.30	2.10	2.10
3	6.75	2.10	2.10	6.85	2.10	2.10	7.20	2.10	2.10	7.05	2.10	2.10	7.20	2.10	2.10
4	7.0	2.10	2.10	7.00	2.10	2.10	7.20	2.10	2.10	6.90	2.10	2.10	7.20	2.10	2.10
5	7.0	2.10	2.10	7.00	2.10	2.10	7.00	2.10	2.10	7.15	2.10	2.10	7.25	2.10	2.10
6	7.0	2.10	2.10	7.20	2.10	2.10	7.00	2.15	2.15	6.95	2.10	2.10	7.20	2.10	2.10
7	7.0	2.10	2.10	7.15	2.10	2.10	7.10	2.10	2.10	7.00	2.10	2.10	7.30	2.10	2.10
8	7.25	2.10	2.10	6.80	2.10	2.10	7.00	2.10	2.10	7.10	2.10	2.10	7.20	2.10	2.10
9	6.9	2.10	2.10	6.90	2.10	2.10	7.40	2.10	2.10	7.00	2.10	2.10	6.90	2.10	2.10
10	6.9	2.10	2.10	6.95	2.00	2.00	7.30	2.10	2.10	6.7	2.10	2.10	7.00	2.25	2.25
11	--	--	--	--	--	--	--	--	--	--	2.10	2.10	--	2.60	2.60
12	--	--	--	--	--	--	--	--	--	--	2.10	2.10	--	6.30	6.30

* ML - Mixed Liquor

A retention time of 1/2 day proved insufficient, as by day ten indications of an impending reactor failure were evident when the effluent pH increased to 2.25. By day eleven, the effluent pH was 2.6 and by day twelve 6.3. At this point the reactor at 1/2 day retention time was considered to have failed, and experimentation was discontinued on this reactor.

Table 29 lists the values of the Mixed Liquor Total Suspended Solids and Mixed Liquor Volatile Suspended Solids.

Sample size used during the retention time study to obtain MLTSS and MLVSS values was 250 ml, taken from the effluent. An aliquot of 250 ml of mixed liquor taken from the reactor would have seriously affected thiosulphate oxidation. As the system was completely mixed without recycle, the TSS and VSS results obtained on the effluent were assumed to apply to the mixed liquor.

At no time did the VSS value exceed the TSS value. However, on several occasions, the values were identical or differed by an amount that could be attributed to analytical erros during weighing.

Table 30 presents values of the effluent turbidity, in Nelphometric Turbidity Units (NTU), for each value of the retention time.

Results are reasonably consistent at each value of the retention time, and could be due to the use of more than the one hour recommended warm-up period. It is not thought to be due to any constancy in MLTSS and MLVSS values, as these values fluctuated considerably. See Table 29.

TABLE 29 MLTSS & MLVSS FOR θ_c VARIATION STUDY

DAY	θ_c = 4 DAYS		θ_c = 3 DAYS		θ_c = 2 DAYS		θ_c = 1 DAY		θ_c = ½ DAY	
	MLTSS*(mg/l)	MLVSS**(mg/l)	MLTSS(mg/l)	MLVSS(mg/l)	MLTSS(mg/l)	MLVSS(mg/l)	MLTSS(mg/l)	MLVSS(mg/l)	MLTSS(mg/l)	MLVSS(mg/l)
1	6.4	5.6	6.8	6.4	6.8	6.8	10.0	10.0	30.0	29.2
2	9.2	8.4	6.4	6.4	7.2	6.4	6.4	---	5.2	4.4
3	12.4	11.6	5.2	4.8	8.8	7.2	6.8	6.0	4.0	4.0
4	10.0	9.6	6.8	6.8	5.6	5.2	4.0	4.0	3.2	---
5	8.8	8.8	7.2	7.2	6.0	5.6	3.6	---	4.0	4.0
6	5.6	5.6	10.4	9.2	4.8	4.0	3.6	3.6	4.8	4.0
7	7.6	7.2	8.8	7.6	6.8	6.8	4.8	3.6	4.8	3.2
8	5.2	5.2	7.6	7.6	12.4	12.4	2.0	2.0	4.4	4.4
3	6.0	6.0	5.2	5.2	13.6	11.2	4.0	3.6	7.2	6.4
10	6.4	5.6	5.2	4.4	9.2	7.6	1.6	1.6	16.8	16.8

* MLTSS - Mixed Liquor Total Suspended Solids

** MLVSS - Mixed Liquor Volatile Suspended Solids

TABLE 30 EFFLUENT TURBIDITY FOR θ_c VARIATION STUDY

DAY	θ_c = 4 DAYS	θ_c = 3 DAYS	θ_c = 2 DAYS	θ_c = 1 DAY	θ_c = ½ DAY
	Effluent Turbidity (NTU)*	Effluent Turbidity (NTU)	Effluent Turbidity (NTU)	Effluent Turbidity (NTU)	Effluent Turbidity (NTU)
1	12	10	12	10	170
2	16	9	15	17	27
3	16	10	14	20	20
4	16	10	14	20	21
5	16	7	14	19	20
6	14	6	14	18	20
7	14	7	14	16	17
8	15	8	10	14	15
9	15	9	9	14	22
10	15	9	9	13	120
11				12	

* NTU - Nelphometric Turbidity Units

Effluent turbidity ranged from 12-16 NTU for the 4 day retention time, 6-10 NTU for the 3 day retention time and 9-15 NTU for the 2 day retention time. For these retention times, the trend is a decreasing value of effluent turbidity with time, except for the 4 day retention time.

At the 1 day retention time, there was a noticeable increase over the turbidity values of the 2 day retention time, with each corresponding day's value at the 1 day retention time being greater than that at 2 days retention time. The increase in turbidity at 1 day retention time is not reflected in increased MLTSS and MLVSS values for this retention time, and neither is it reflected in a decreased reactor performance with respect to thiosulphate oxidation (see Table 32 for thiosulphate oxidation), although there is a decrease in COD removal compared with that at the 2 day retention time (see Table 31 for COD removal data).

At the 1/2 day retention time, there was an immediate increase in effluent turbidity, to 170 NTU on day one, which coincided with an increase in MLTSS and MLVSS values. Even though the turbidity had decreased to 27 NTU on day two, during this retention time the turbidity was consistently greater than at any of the previous retention times. The increase in turbidity on day ten over the value of day nine signified an imminent failure. After day ten, turbidity was not monitored for the 1/2 day retention time, beyond a daily visual inspection, but was noticed to decrease so that by day twelve the mixed liquor appeared colourless.

Table 31 summarizes the influent and effluent COD values and percent COD removals for the retention time study.*

A comparison of influent COD shows that these values were reasonably similar for each retention time study, and in the majority of cases above 500 mg/l. During the 2 day, 1 day and 1/2 day retention time studies, influent COD occasionally fell below 500 mg/l with the lowest recorded value being 446.0 mg/l, on day three of the 1 day retention time study.

Effluent COD remained consistently below 50 mg/l for the duration of the 4 day, 3 day, and 2 day retention time studies. For the 1 day retention time study, effluent COD was below 50 mg/l on day one and two, but increased to over 60 mg/l by day three, and remained above 50 mg/l until day nine.

For the 1/2 day retention time study, effluent COD increased sharply to nearly 70 mg/l on day one, recovered to nearly 50 mg/l on day three, and remained above 50 mg/l for the duration of the run, until day ten. After day ten no further monitoring was performed on the 1/2 day retention time study, and although the effluent COD value on day ten did not indicate reactor failure, other parameters, such as turbidity and effluent pH, did.

Percentage COD removals paralleled the effluent COD values. During the 4 day, 3 day and 2 day retention time studies, COD removal always bettered 91 percent. For the 1 day retention time study, after initial COD removals exceeding 91 percent, the performance decreased somewhat, and COD removal fluctuated between about 85 and 90 percent.

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* Figures 13 to 17 illustrate graphically the variations of influent and effluent COD for the 4,3,2,1,1/2 day retention time studies, and Figure 18 compares the effluent COD values for these retention times.

TABLE 31 INFLUENT AND EFFLUENT COD AND PERCENT COD REMOVAL FOR θc VARIATION STUDY

DAY	θc = 4 DAYS			θc = 3 DAYS			θc = 2 DAYS			θc = 1 DAY			θc = ½ DAY		
	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (mg/l)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (mg/l)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (mg/l)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (mg/l)	Influent COD (mg/l)	Effluent COD (mg/l)	Removal COD (mg/l)
1	539.0	43.0	92.09	537.0	41.0	92.42	525.0	37.0	92.98	521.0	37.0	92.94	512.0	70.0	86.36
2	539.0	46.5	91.37	537.0	37.0	93.14	552.0	46.5	91.58	517.0	43.0	91.76	518.5	67.0	87.12
3	539.0	46.5	91.37	537.0	33.0	93.86	537.0	39.0	92.78	446.0	61.0	86.34	518.5	65.0	87.50
4	541.0	43.0	92.11	537.0	29.0	94.58	504.0	43.0	91.54	448.0	69.0	84.65	522.0	67.0	87.22
5	535.0	43.0	92.03	537.0	25.0	95.31	485.0	43.0	91.20	513.0	67.0	86.97	522.0	63.0	87.97
6	550.0	48.5	91.20	547.0	27.0	95.04	498.0	45.0	91.05	507.0	61.0	87.98	499.0	57.0	88.58
7	537.0	35.0	93.5	537.0	23.0	95.67	521.0	43.0	91.82	477.0	53.0	88.89	495.0	64.0	87.06
8	502.0	41.0	91.89	502.0	35.0	93.05	515.5	31.0	93.98	488.0	56.0	88.45	503.0	54.0	84.19
9	508.0	45.0	91.22	508.0	31.0	93.89	515.5	27.0	94.74	485.5	58.0	88.00	485.5	50.5	89.60
10	501.0	43.0	91.50	506.0	31.0	93.87	519.0	31.0	94.03	462.0	49.0	89.50	493.0	50.5	89.76

Figure (13). Influent and Effluent COD values for $\theta_c = 4$ days

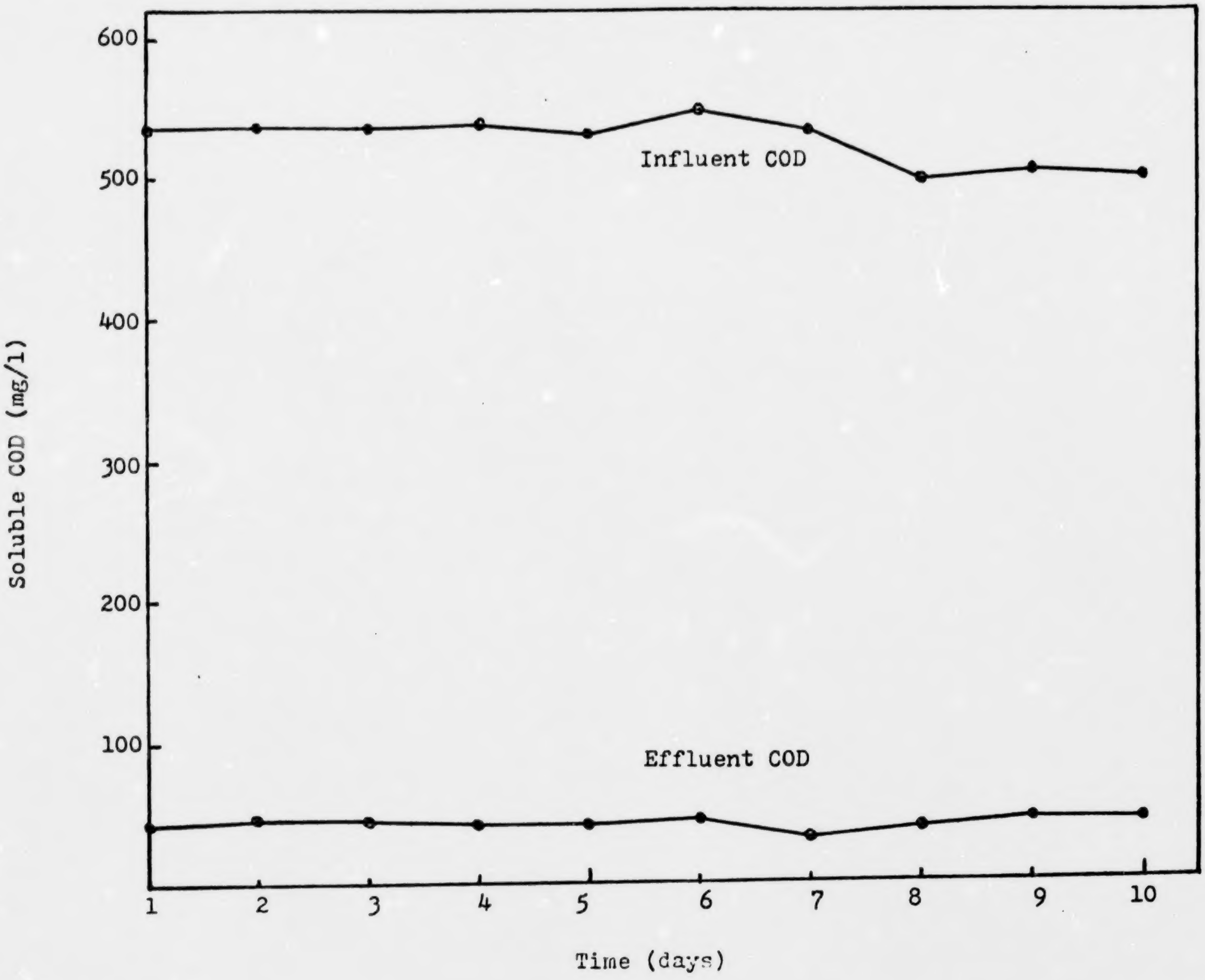


Figure (14). Influent and Effluent COD values for $\theta_c = 3$ days

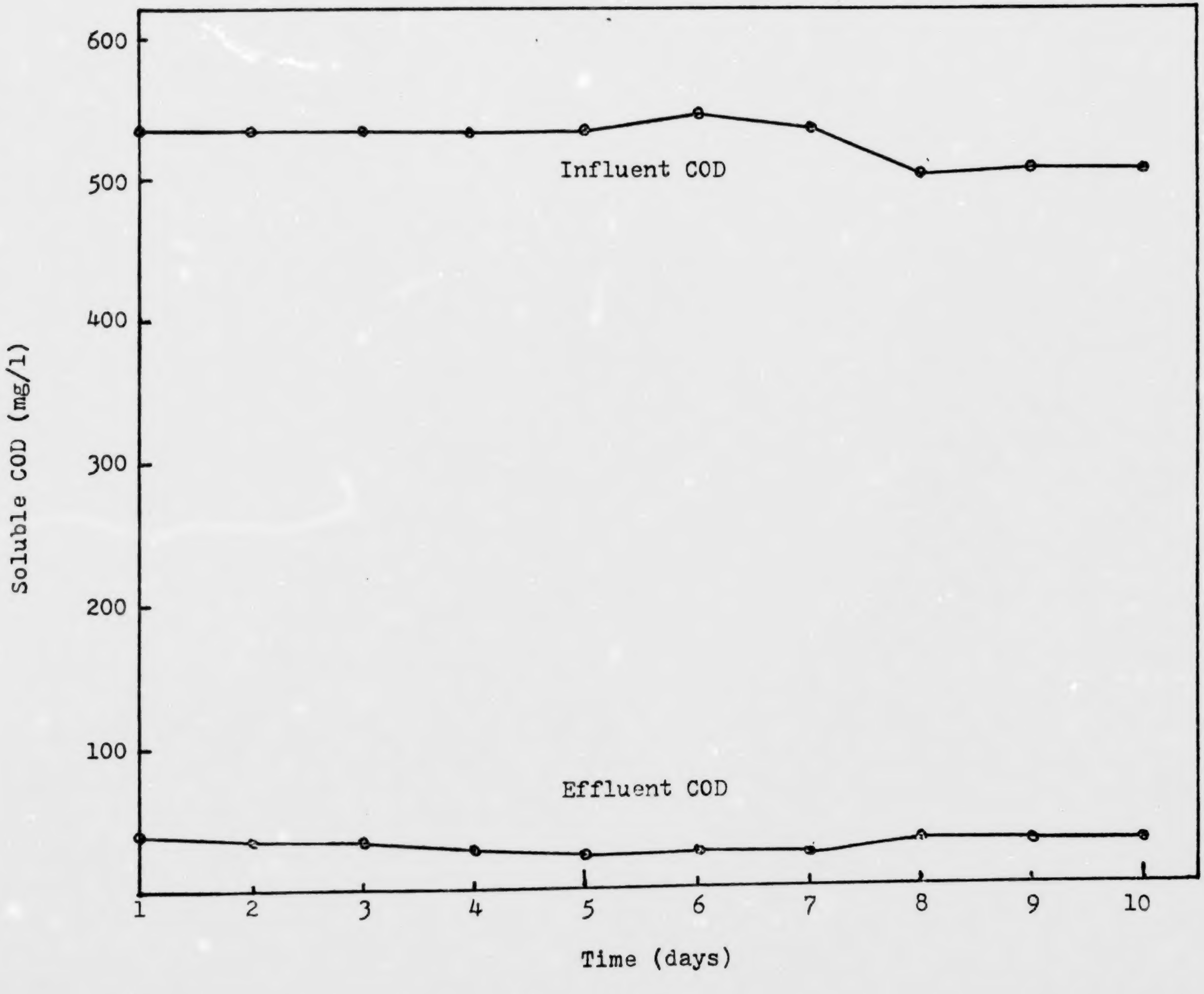


Figure (15). Influent and Effluent COD values for $\theta_c = 2$ days

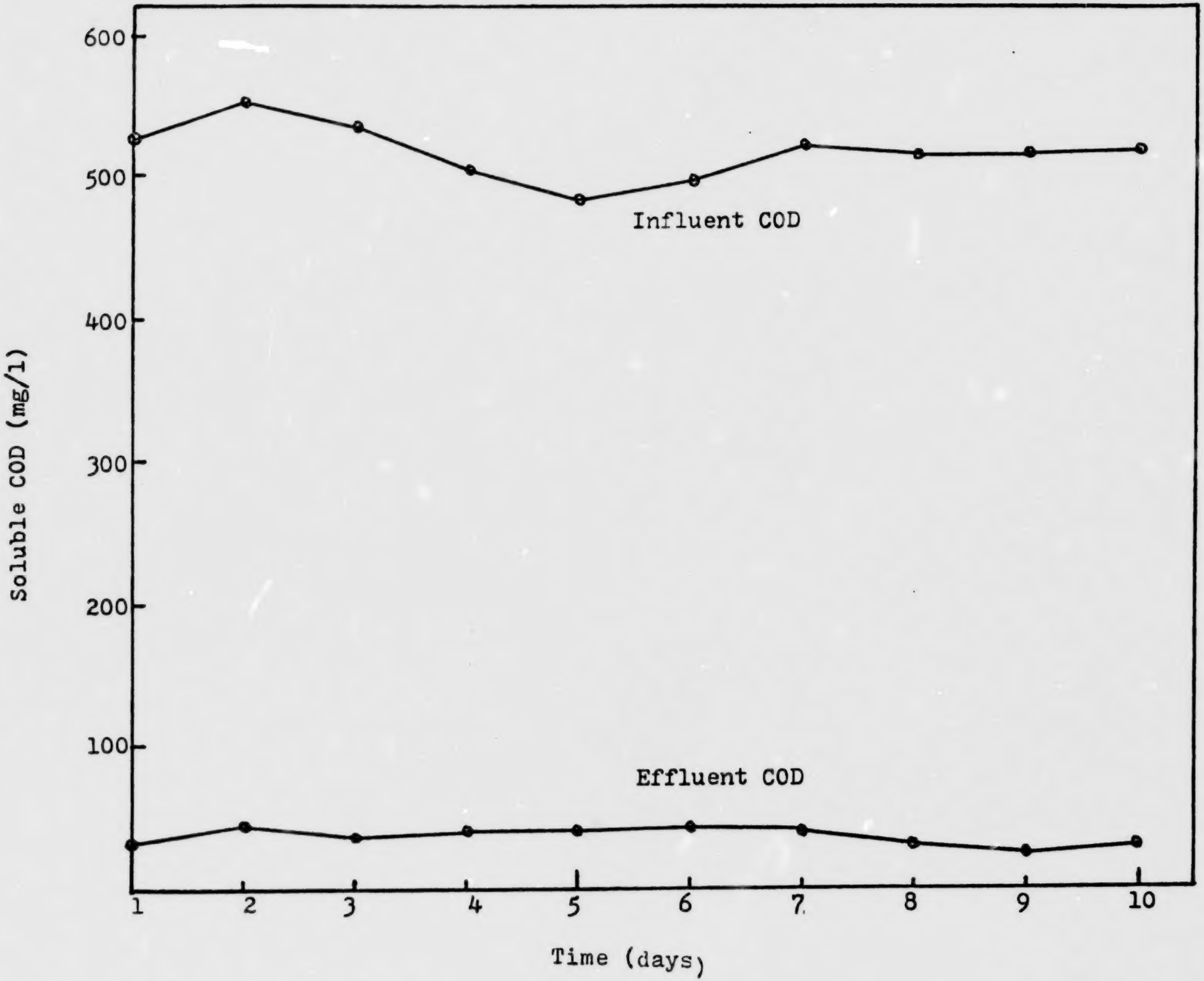


Figure ((16). Influent and Effluent COD values for $\theta_c = 1$ day

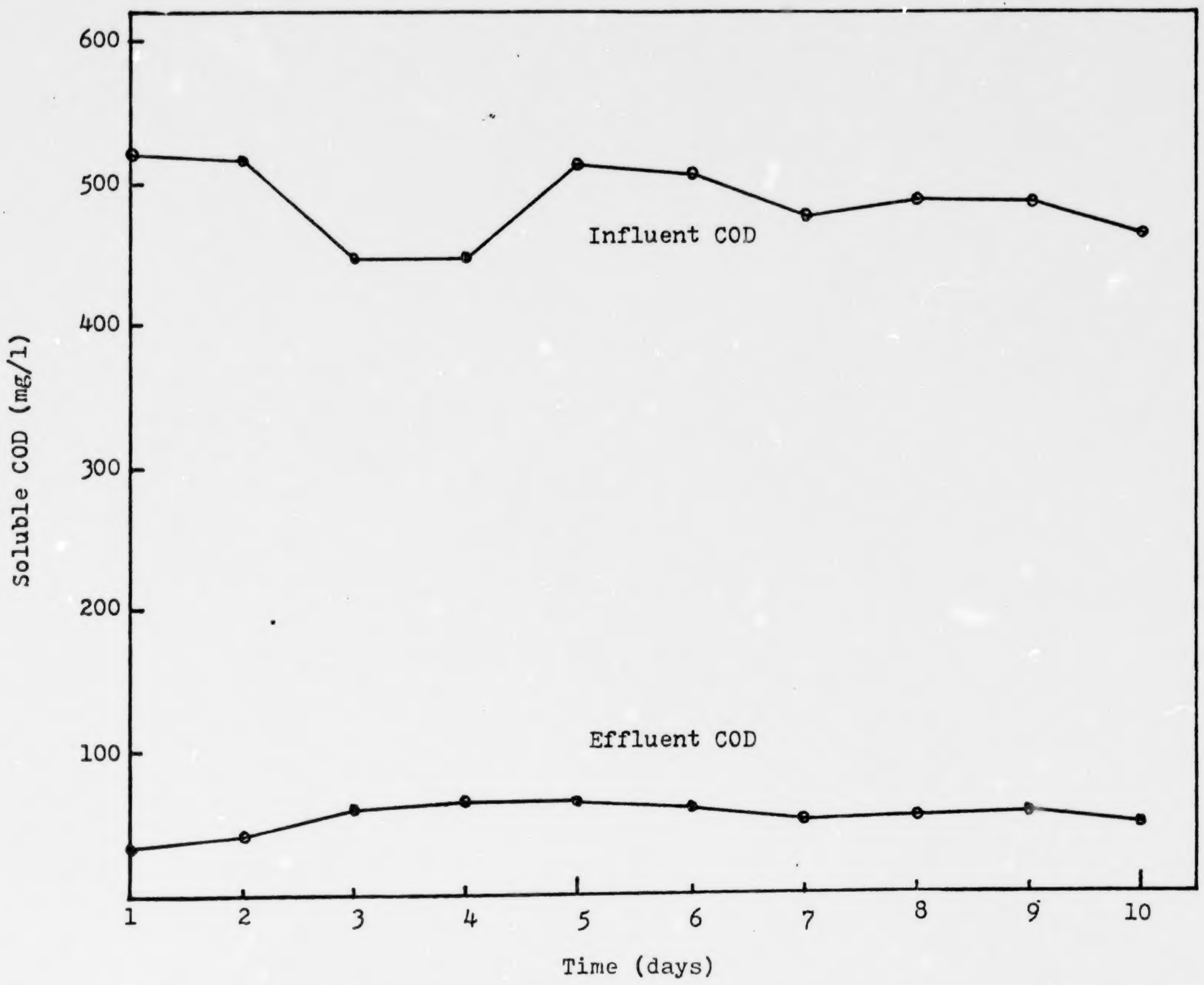


Figure (17). Influent and Effluent COD values for $\theta_c = \frac{1}{2}$ day

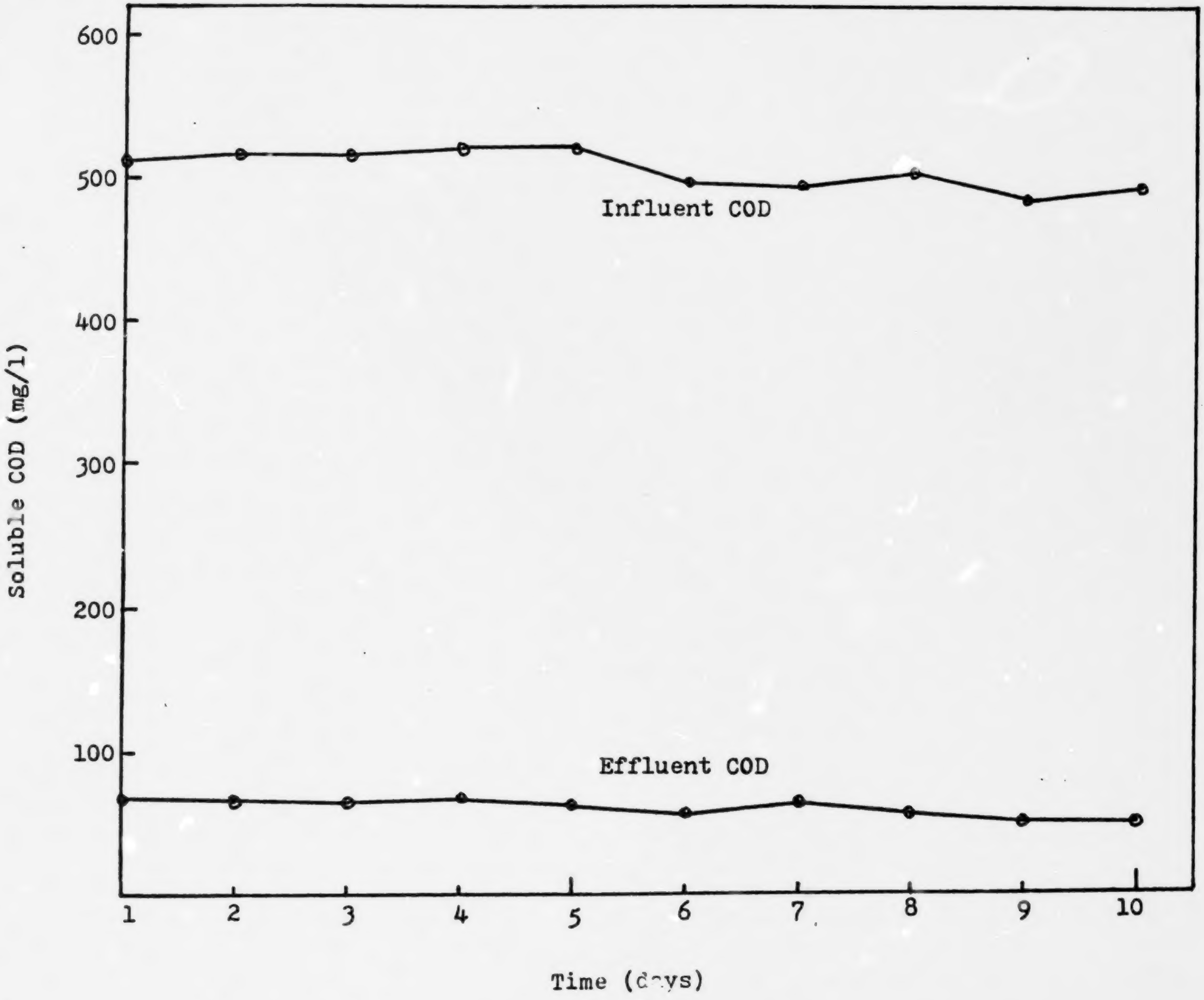
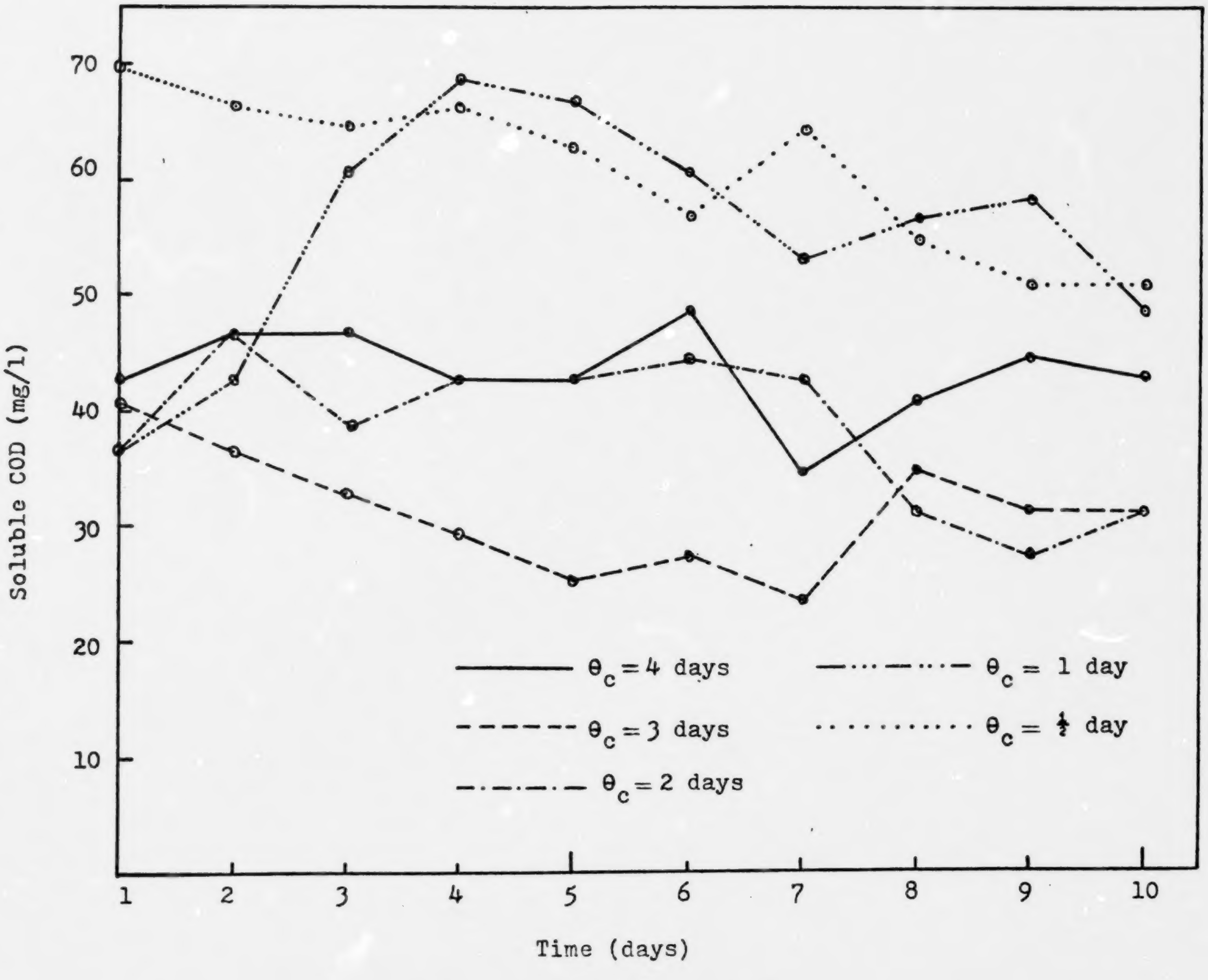


Figure (18). A Comparison of Effluent COD for $\theta_c = 4, 3, 2, 1, \frac{1}{2}$ days



For the 1/2 day retention time study, COD removal did not exceed 90 percent at any time. The difference, however, between percent COD removals for the 1 day and 1/2 day retention time studies, after day two, is not significantly different, with the greatest difference being nearly 3 percent.

Table 32 presents influent and effluent thiosulphate concentration for the retention time studies. As with the phosphorous variation study, 2,000 mg of $Na_2S_2O_3.5H_2O$ were added per litre of influent, resulting in a theoretical thiosulphate concentration of 904 mg/l. Influent thiosulphate concentrations, however, were not near this theoretical value during any of the retention time studies. This dissimilarity between the theoretical and actual influent thiosulphate concentrations was also noted during the phosphorous variation study.

Influent thiosulphate concentration usually varied between 680 mg/l and 710 mg/l, with some exceptions.

Effluent thiosulphate concentration was, for the 4 day, 3 day and 2 day retention time studies, constant at 3.0 mg/l, throughout the duration of each study. For the 1 day retention time study, effluent thiosulphate concentration increased to 3.5 mg/l on day one, but by day two had decreased to 3.0 mg/l, a value maintained until day ten. Similarly, for the 1/2 day retention time study, effluent thiosulphate increased to 6.0 mg/l on day one, but by day two had decreased to 3.0 mg/l, a value maintained until day ten. Although the 1/2 day retention time study failed on day ten, effluent thiosulphate concentration was not monitored beyond day ten.

TABLE 32 INFLUENT AND EFFLUENT $S_2O_3^{2-}$ CONCENTRATIONS FOR θc VARIATION STUDY

DAY	θc = 4 DAYS		θc = 3 DAYS		θc = 2 DAYS		θc = 1 DAY		θc = ½ DAY	
	$S_2O_3^{2-}$ Influent (mg/l)	Effluent (mg/l)	$S_2O_3^{2-}$ Influent (mg/l)	Effluent (mg/l)	$S_2O_3^{2-}$ Influent (mg/l)	Effluent (mg/l)	$S_2O_3^{2-}$ Influent (mg/l)	Effluent (mg/l)	$S_2O_3^{2-}$ Influent (mg/l)	Effluent (mg/l)
1	692.0	3.0	685.0	3.0	692.0	3.0	692.0	3.5	699.0	6.0
2	702.0	3.0	695.0	3.0	692.0	3.0	702.0	3.0	718.0	3.0
3	695.0	3.0	695.0	3.0	692.0	3.0	650.0	3.0	695.0	3.0
4	699.0	3.0	692.0	3.0	692.0	3.0	699.0	3.0	713.0	3.0
5	681.0	3.0	695.0	3.0	692.0	3.0	702.0	3.0	695.0	3.0
6	697.0	3.0	688.0	3.0	694.0	3.0	692.0	3.0	692.0	3.0
7	692.0	3.0	692.0	3.0	704.0	3.0	664.0	3.0	678.0	3.0
8	694.0	3.0	699.0	3.0	692.0	3.0	660.0	3.0	685.0	3.0
9	692.0	3.0	694.0	3.0	702.0	3.0	657.0	3.0	650.0	3.0
10	694.0	3.0	694.0	3.0	711.0	3.0	629.0	3.0	664.0	3.0

Table 33 summarizes the effluent polythionate concentrations (expressed as mg/l $S_2O_3^{2-}$) for the retention time study. Influent polythionate concentration was assumed to be zero mg/l at all times. This assumption, however, was not checked. Figure 19is a comparison of effluent polythionate concentrations for each value of retention time.

This figure shows that, with the exception of the 4 day retention time study, which showed a few inconsistent points, and the 1/2 day retention time study, which failed after ten days and is thus an unreliable guide, the values for the 3 day, 2 day and 1 day retention time studies were, after day one, all fairly linear, between day two and day ten. Neither is there any trend of simultaneous rising and falling of values as noted in the phosphorous variation study.

Omitting the day one value from the 3 day retention time study, the difference between the highest and lowest values of effluent polythionate was about 8 mg/l. For the 2 day retention time study, this difference was about 14 mg/l, and for the 1 day retention time study, omitting the day one value, the difference was about 10 mg/l.

These values are more consistent than those of the phosphorous variation study, see Table 24 and Figure 11 , and are attributed to an improved monitoring during the polythionate determination whereby the heating of the sample, containing polythionates, with mercuric chloride, the process during which acid is produced giving a measure of polythionate production, was carefully watched, thus ensuring a more consistent heating. This would also explain the reasonable linearity of Figure 19.

TABLE 33 EFFLUENT POLYTHIONATE CONCENTRATIONS FOR θc VARIATION STUDY

DAY	θc = 4 DAYS	θc = 3 DAYS	θc = 2 DAYS	θc = 1 DAY	θc = ½ DAY
	Effluent Polythionates (mg/l) as $S_2O_3^{2-}$	Effluent Polythionates (mg/l) as $S_2O_3^{2-}$	Effluent Polythionates (mg/l) as $S_2O_3^{2-}$	Effluent Polythionates (mg/l) as $S_2O_3^{2-}$	Effluent Polythionates (mg/l) as $S_2O_3^{2-}$
1	5.0	17.0	33.0	9.0	153.0
2	33.0	34.0	34.0	29.0	27.0
3	16.0	38.0	27.0	29.0	18.0
4	31.0	34.0	33.0	32.0	21.0
5	38.0	29.0	35.0	22.0	23.0
6	9.0	34.0	33.0	26.0	24.0
7	28.0	28.0	21.0	27.0	26.0
8	27.0	34.0	29.0	28.0	25.0
9	22.0	31.0	34.0	25.0	51.0
10	32.0	33.0	31.0	30.0	42.0

Figure [illegible]. Comparison of Effluent Polythionate Concentration for θ_c = [illegible] days

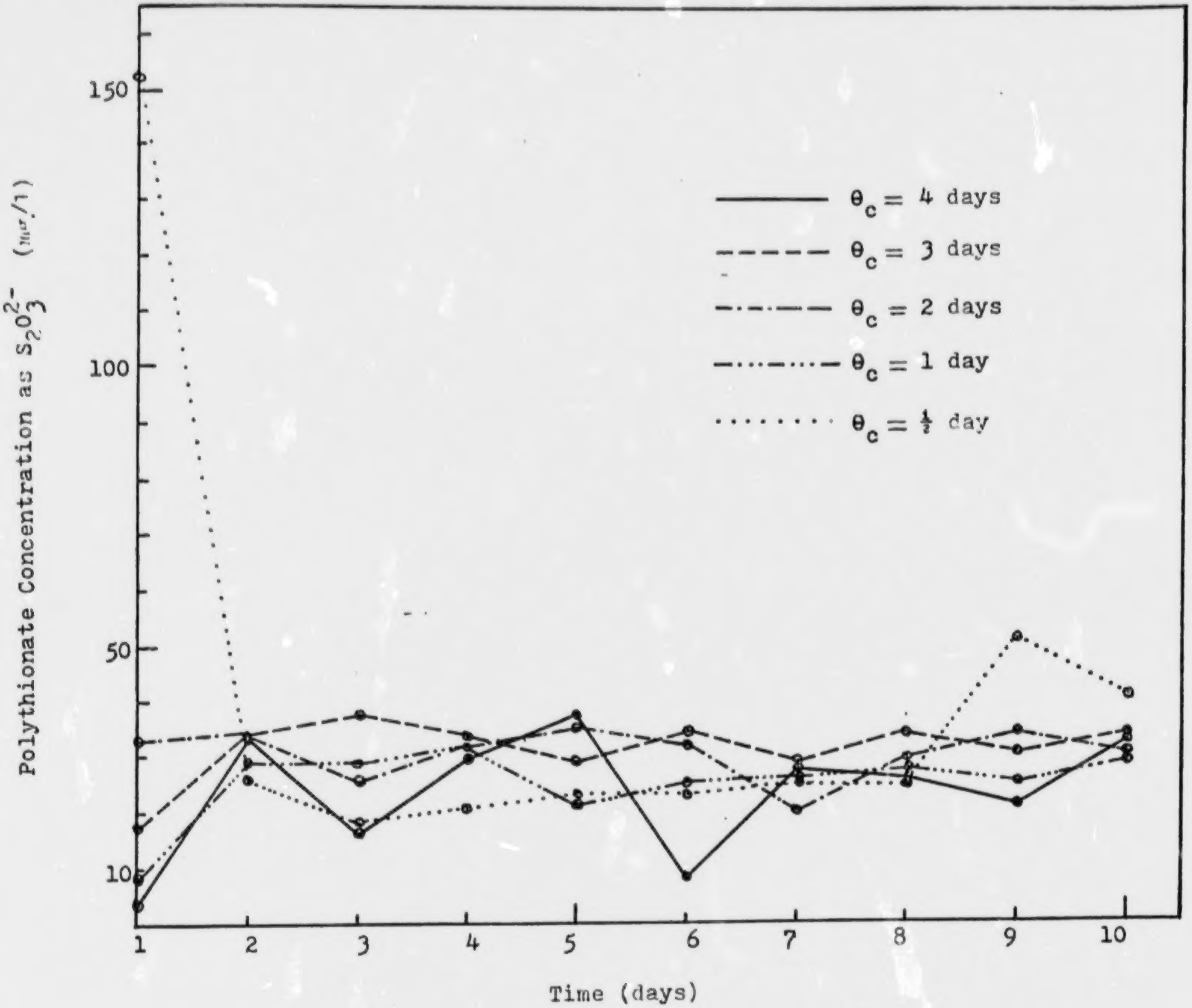


Table 34 presents the influent and effluent sulphate concentrations for the retention time study.

The influent sulphate concentration, sources of which were the trace element solution and tap water, was constant at 60 mg/l during each retention time study. This constancy is, possibly, due to the sensitivity of the analytical procedure used for sulphate.

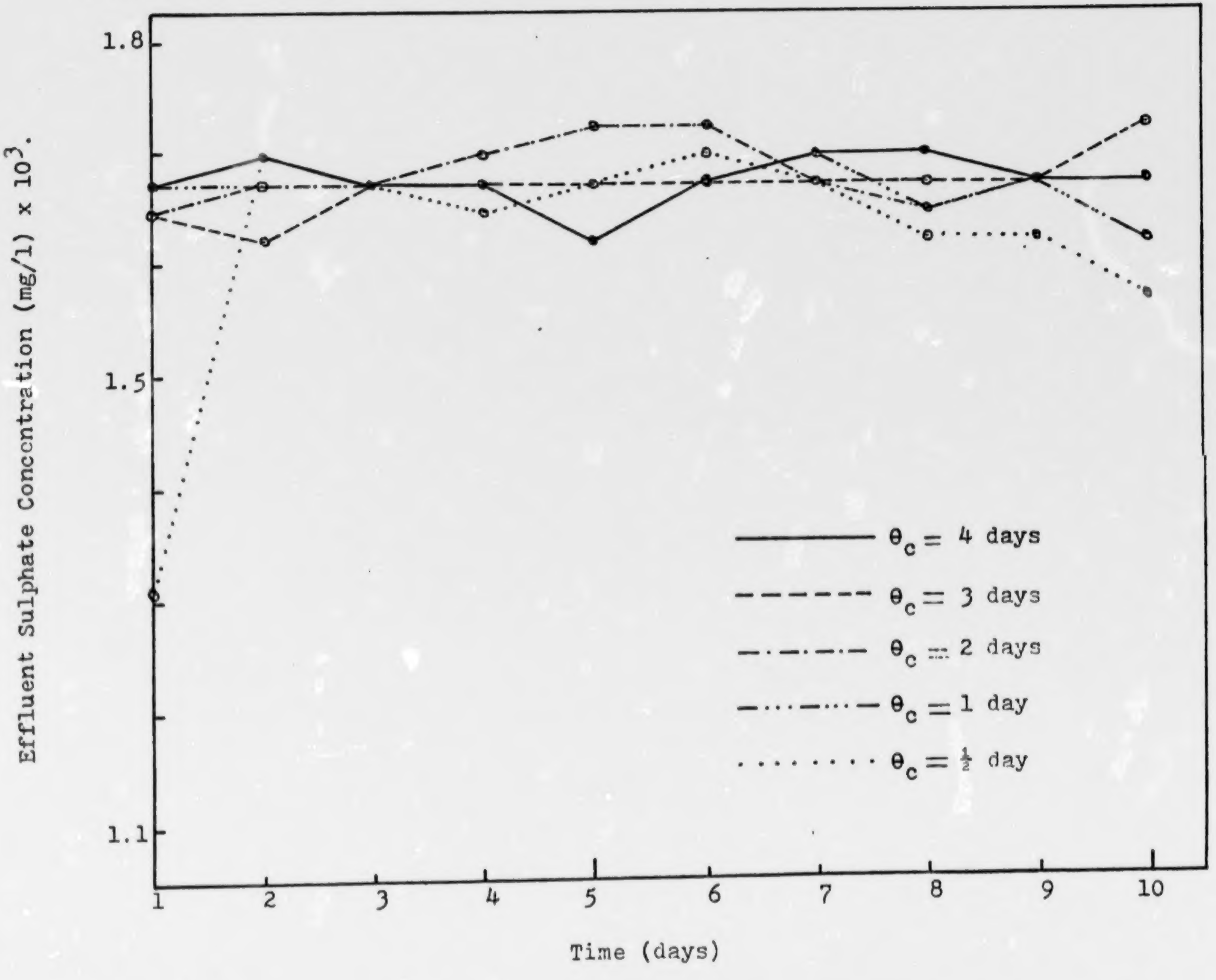
Effluent sulphate concentrations during each retention time study, are also fairly consistent, being concentrated in a band no more than 100 mg/l wide, as shown in Figure 20, a comparison of effluent sulphate concentrations.

The difference between maximum and minimum effluent sulphate concentrations for the retention time studies are: 78 mg/l (4 day retention time), 52 mg/l (3 day retention time), 128 mg/l (2 day retention time) and 78 mg/l (1 day retention time). For the 1/2 day retention time study, the "shock effect" of changing to this retention time, can be seen on day one, when the effluent sulphate decreased to 1310 mg/l. The reactor recovered to 1698 mg/l on day two, and maintained effluent sulphate concentrations comparable to the 4 day, 3 day, 2 day and 1 day retention time studies up to day nine. After day ten, monitoring of effluent sulphate for the 1/2 day retention time study was not continued, but the impending failure was indicated with the decrease in the day ten value of effluent sulphate to 1568 mg/l.

TABLE 34 INFLUENT AND EFFLUENT SULPHATE CONCENTRATIONS FOR θ_c VARIATION STUDY

	θ_c = 4 DAYS		θ_c = 3 DAYS		θ_c = 2 DAYS		θ_c = 1 DAY		θ_c = ½ DAY	
DAY	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)	Influent SO_4 (mg/l)	Effluent SO_4 (mg/l)
1	60	1672	60	1646	60	1646	60	1672	60	1310
2	60	1698	60	1620	60	1672	60	1672	60	1698
3	60	1672	60	1672	60	1672	60	1672	60	1672
4	60	1672	60	1672	60	1698	60	1672	60	1646
5	60	1620	60	1672	60	1724	60	1620	60	1672
6	60	1672	60	1672	60	1724	60	1672	60	1698
7	60	1698	60	1672	60	1672	60	1698	60	1672
8	60	1698	60	1672	60	1646	60	1645	60	1620
9	60	1672	60	1672	60	1672	60	1672	60	1620
10	60	1672	60	1724	60	1672	60	1620	60	1568

Figure (20). A Comparison of Effluent Sulphate Concentrations for $\theta_c =$ 4,3,2,1, ½ days



CHAPTER (6): DISCUSSION

6.1 Influent Phosphorous Variation Study

With the values of influent phosphorous used in this study (values which exceeded the estimated minimum phosphorous requirement), there was very little difference noted between the effluent characteristics of Reactors (1), (2) and (3).

Although influent pH values varied between the reactors (from Reactor (1) which recorded consistently greater influent pH values than Reactors (2) and (3), through to Reactor (3) which recorded consistently lower influent pH values than Reactors (1) and (2)), Mixed liquor and effluent pH values were consistently at pH 2.0. The similarity of mixed liquor and effluent pH values is accounted for by the complete mix without recycle system used. The variation of influent pH values it attributed to the acidic nature of potassium di-hydrogen phosphate (KH_2PO_4) used as the source of phosphorous. (A 5 percent KH_2PO_4 solution at 25°C has a pH of 4.2).

Influent pH values recorded during this study vary by as much as about 1.0 pH unit less than to 3.0 pH units greater than influent pH values noted by other experimenters. Kreye, et al., [14,15]reported influent pH values of 8.4 and 8.6 during two studies, with effluent pH values from pH 2.7 to as low as pH 1.6. Influent phosphorous concentration during these studies were 5.5 mg/l PO_4-P and 14.0 mg/l PO_4-P . A report by BC Research (3) does not state influent pH values, but reports effluent pH values in the range pH 1.7 to 2.1, depending on the influent thiosulphate concentrations and residence time. They report batch studies, however, as showing a final pH in the range 1.7 to 1.9 regardless of initial pH of 3,4 or 5. Schmidt (22) reported an effluent pH of 2.0 with an influent pH of 4.0.

In general, effluent pH will depend on influent thiosulphate concentration as the resulting oxidation to SO_4^{2-} and H^+ will determine the final pH value.

Mixed Liquor Total Suspended Solids and Mixed Liquor Volatile Suspended Solids show no effects of the varying influent phosphorous concentrations. Results are inconsistent in that on occasions for each reactor MLVSS values exceeded MLTSS values. This inconsistency is thought to be due to the low solids and biomass production together with the sample size of 25 ml used for the MLTSS and MLVSS analyses. As the sample was taken from the reactor contents, volumes were limited to 25 ml, as anything greater would, it is believed, have interfered with the oxidation process.

No conclusions can be reached regarding the effects of influent phosphorous on MLTSS and MLVSS values due to the inconsistencies obtained.

Low TSS and VSS values seem characteristic of thiosulphate oxidizing systems, even with an adequate supply of phosphorous and nitrogen. Leclair (16) reports a Rotating Biological Contactor study during which the effluent suspended solids was consistently less than 10 mg/l throughout the study. Schmidt (22) reports problems with Volatile Suspended Solids analyses and obtained inconsistent results with MLVSS tests, the conventional representation of biomass. He attributes this inconsistency to a colloidal suspension in the reactor which was presumed to be, but not tested for, elemental sulphur. LeClair (16) also obtained "an appreciable amount of white colloidal sulphur", but was more positive as the nature of the colloid. Elemental Sulphur, if present, would interfere with the total and volatile suspended solids determination, as it liquifies at 160°C (25), well below the temperature of 550°C required for VSS analyses.

During the phosphorous variation study, a colloidal suspension was also noted in the reactor. When a sample of mixed liquor was passed through a filter, a yellow coloured residue on the filter was observed. This was thought to be elemental sulphur, although not tested for.

Kreye, et al. (14,15), obtained higher MLVSS values than did LeClair (16) and Schmidt (21) with the lowest value about 100 mg/l. These unusually high values are attributed to the addition of sewage to the influent containing thiosulphate in an attempt to promote, simultaneously, both thiosulphate oxidation and the oxidation of organic compounds contained in sewage. Their values of MLVSS is not considered an adequate indication of MLVSS for a system oxidizing only thiosulphate.

During the phosphorous variation study, algae (Anabena) was observed growing on the walls of all reactors. This algal growth could also have interfered with the VSS determinations.

A possible alternative to MLTSS and MLVSS determinations is an accurate determination of effluent turbidity. Effluent turbidity evaluations, it was found, gave a quick, qualitative estimation of how efficiently a reactor was functioning. In the phosphorous variation study, effluent turbidity values for the three reactors fluctuated greatly. However, it was noted that Reactor (1) usually showed, on comparison with Reactor (2) and Reactor (3), lower effluent turbidity values. Apart from the high MLTSS and MLVSS and effluent turbidity values on day two, these fluctuations in turbidity values did not correspond to the fluctuations in the MLTSS and MLVSS values.

These fluctuations, as remarked earlier, were attributed to an unsufficient "warm-up" time for the instrument. However, when the three reactors were functioning efficiently, effluent turbidity values did not exceed 20 NTU.

Effluent turbidity evaluations can usefully predict imminent reactor failure, when it was observed that increases in turbidity preceeded reactor failure. This is shown in Table 21 , when on day fourteen effluent turbidity for Reactor (3) was 1000 NTU. Following this high turbidity value, on day fifteen mixed liquor and effluent pH was 2.25 (an increase over the day fourteen value of 2.10) which from this point on increased until reactor failure occurred.

Figure 21 shows the turbidity of Reactor (3) in comparison with Reactors (1) and (2) on day sixteen of the phosphorous variation study. Noticeable, is the lower turbidity of Reactor (3). When this photograph was taken, Reactor (3) was considered to have failed.

No qualitative values of effluent turbidity were found, in the literature, for other studies.

Figure (21) A comparison of the mixed liquor turbidities of Reactor (1), top, Reactor (2), centre, and Reactor (3), bottom, on day sixteen of the influent phosphorous variation study. On the day these photographs were taken, Reactor (3) was considered to have failed due to the clarity of the mixed liquor. Reactors (1) and (2), however, were still functioning efficiently. Lack of mixed liquor turbidity is indicative, in general, of reactor failure.

COD removals for Reactors (1) and (2), after day three and for the remainder of the study, was better than 91 percent. Reactor (3) exhibited a slightly better removal performance between day three and day fifteen than did Reactors (1) and (2). After day fifteen, however, Reactor (3) failed, as the increasing effluent COD values indicate.

Based on these results, it would appear that the larger influent phosphorous concentration resulted in a marginally better performance. However, the reactor receiving the largest influent phosphorous concentration was the only one of the three that failed.

Graham (11) reported good Permanganate Value removals at influent phosphate concentrations of 120 mg/l PO_4 (39 mg/l PO_4-P) and 60 mg/l PO_4 (19.5 mg/l PO_4-P) using complete mix reactors without recycle to oxidize thiosulphate wastes from ammonical effluents produced from coal carbonizing systems. These ammonical effluents were supplemented with thiosulphate in various concentrations. Graham reported PV removals varying from 83.2 to 93.7 percent depending on the source of ammonical effluent and the amount of thiosulphate added. For synthetically prepared thiosulphate wastes, Graham reported PV removals of 98.6 percent, with 3000 mg/l $S_2O_3^{2-}$ and 91.7 percent with 10,000 mg/l $S_2O_3^{2-}$.

Kreye, et al. (15), however, did not report good COD removals when compared with the PV reductions reported by Graham. COD removals of less than 50 percent characterized one of their studies with influent phosphorous at 5.5 mg/l PO_4-P and thiosulphate varied from 1500 mg/l to 4000 mg/l. The low COD removal is attributed to the presence of domestic sewage in the influent. In a second study, domestic sewage in the influent was retained, influent phosphorous was increased to 14 mg/l PO_4-P and influent thiosulphate concentration varied from 1500 mg/l to 4000 mg/l. From the work of Kreye, et al., it would appear that increased influent phosphorous concentrations improved COD removals.

This is partially substantiated by the results of this Study. As a final comment on effluent COD values, it should be noted that effluent COD, by definition of COD, is composed of the unoxidized sulphur compounds remaining in the effluent. Specifically, effluent thiosulphate and effluent polythionates.

However, the sum of effluent thiosulphate and effluent polythionate concentrations did not agree with the values of effluent COD when effluent COD was expressed as $S_2O_3^{2-}$ (by multiplying COD values by 0.57 mg COD/mg $S_2O_3^{2-}$, the relation between $S_2O_3^{2-}$ and theoretical COD; this was obtained from stoichiometric considerations of thiosulphate oxidation to sulphate).

Effluent COD concentrations, as $S_2O_3^{2-}$, were greater than the sum of effluent thiosulphate and effluent polythionate concentrations. This lack of agreement was observed for the duration of the phosphorous variation study, for all reactors, and is attributed to analytical problems for both thiosulphate and the polythionates. The COD analysis, as per Standard Methods, is considered to be a more exact expression of unoxidized sulphur compounds.

Closely related to the Chemical Oxygen Demand and the constituent in the influent responsible for COD exertion, was thiosulphate. Although thiosulphate was added in concentrations of

2000 mg/l $Na_2S_2O_3.5H_2O$ per litre of influent, resulting in a theoretical influent $S_2O_3^{2-}$ concentration of 904 mg/l, the analytical procedure used for $S_2O_3^{2-}$ determination never measured this theoretical amount. Influent $S_2O_3^{2-}$ concentrations usually varied between 680 mg/l and 730 mg/l for the three reactors. This discrepancy is too large to be attributed solely to experimental errors. A possible explanation, however, could be the partial oxidation of thiosulphate, in the influent jug, to polythionates, with the total COD value remaining constant. Also, unmanifested analytical problems could have accounted for some of this discrepancy.

Effluent thiosulphate concentrations for the three reactors, however, was consistently 3.0 mg/l (after day three) for the duration of the study for Reactors (1) and (2). For Reactor (3), effluent $S_2O_3^{2-}$ concentration was 3.0 mg/l up to day eighteen, increasing to 3.5 mg/l on day nineteen and 4.5 mg/l on day twenty. Reactor (3) is considered to have failed on day fifteen as the increasing values of effluent COD and pH and decreasing values of effluent turbidity indicate.

Percentage thiosulphate removals, accordingly, were very good after day three and up to day twenty, for Reactors (1) and (2) which during this time were above 99 percent. Reactor (3) exhibited over 99 percent thiosulphate removal up to day eighteen.

From these values, it is concluded that phosphorous concentrations had very little effect on effluent thiosulphate concentrations when the reactors were functioning efficiently, as all reactors showed the same effluent thiosulphate concentration.

Other experimenters also reported good thiosulphate removals.

Graham (11) reported 100 percent thiosulphate removal in several studies with ammonical effluents containing thiosulphate in concentrations from 980 mg/l to 3670 mg/l. Phosphorous was supplied at 60 mg/l PO_4 (19.5 mg/l PO_4-P) for the duration of these studies.

Schmidt (22) reported 100 percent $S_2O_3^{2-}$ removal from an influent containing 1000 mg/l $S_2O_3^{2-}$. Phosphorous supply, however, was not stated. A relation between COD and thiosulphate concentration is obtained from a consideration of the equation for thiosulphate oxidation:

$$S_2O_3^{2-} + 2O_2 + H_2O \rightarrow 2SO_4^{2-} + 2H^+,$$

from which 112 mg $S_2O_3^{2-}$ require 64 mg O_2 (for complete conversion to sulphate) or, re-expressing, 0.57 mg O_2/mg $S_2O_3^{2-}$. As the oxygen requirement is analagous to COD the reation can be expressed as 0.57 mg COD/mg $S_2O_3^{2-}$ from which,

$$\text{mg/l } S_2O_3^{2-} \doteq \left[\text{mg/l COD}/0.57 \, \frac{\text{mg COD}}{\text{mg } S_2O_3^{2-}}\right]$$

Using this relation, by way of illustration, with the day five influent and effluent COD and influent and effluent thiosulphate concentrations for Reactor (1) shows the lack of agreement between the value of influent $S_2O_3^{2-}$ concentration, as obtained from the stoichiometric relation above, and the value obtained by idiometric titration.

DAY	INFLUENT		EFFLUENT		COD	
					INFLUENT	EFFLUENT
	$S_2O_3^{2-}$ (mg/l) (by titration)	$S_2O_3^{2-}$ (mg/l) (by SR*)	$S_2O_3^{2-}$ (mg/l) (by titration)	$S_2O_3^{2-}$ (mg/l) (by SR*)	(titration) (mg/l)	(titration) (mg/l)
5	694.0	926.0	3.0	56.0	528.0	32.0

* SR = Stoichiometric Relation, i.e., $S_2O_3^{2-}$ (mg/l) = $\frac{\text{COD(mg/l)}}{0.57}$

Influent thiosulphate concentration by idiometric titration is less than that by stoichiometric considerations. This lack of agreement, remarked on earlier, is noted for all days of the phosphorous variation study and is attributed to errors in the analytical procedure for thiosulphate and possible oxidation of thiosulphate to polythionates during storage in the influent feed jug. Total COD would, of course, remain constant. (As no polythionate analysis was performed on the influent, it is difficult to prove this assertion. Some guidance, however, is provided by Sinha and Walden (26) who showed that in the presence of forced aeration and in the absence of Thiobacillus sp., polythionates can form from thiosulphate. Due to the absence of both forced aeration and Thiobacillus sp. from the influent, it is therefore considered that polythionates were absent from the influent).

If, however, the theoretical influent thiosulphate concentration is used, i.e., 904 mg/l, then the

$$\begin{array}{l}\text{theoretical influent COD}\\ \text{(for day five, Reactor(1))}\end{array} = \left(904\ \frac{\text{mg}}{\text{l}}\ S_2O_3^{2-} \times 0.57 \frac{\text{mg COD}}{\text{mg } S_2O_3^{2-}}\right)$$

$$= 515.0 \text{ mg/l},$$

which is in close agreement with the influent COD value (for day five) namely 528.0 mg/l, and substantiates the argument that the thiosulphate analysis could have been in error.

Similarly, considering day five Reactor (1), effluent thiosulphate values by idiometric titration (3.0 mg/l) is less than that by stoichiometric considerations (56.0 mg/l). This is noted throughout the duration of the phosphorous variation study. This difference, however, could be reasonably explained by the presence of unoxidized polythionates present in the effluent which would contribute to the COD values. However, the difference between 56.0 mg/l (effluent $S_2O_3^{2-}$ obtained from the effluent COD concentration) and 3.0 mg/l (effluent $S_2O_3^{2-}$ concentration by idiometric titration) is too great to be solely attributed to polythionate production, and thus analytical errors for both thiosulphate and polythionates may be responsible.

Although microbiological studies indicated that polythionates, especially tetrathionate $S_4O_6^{2-}$, accumulate in the absence of inorganic phosphate and that the rate of thiosulphate oxidation decreases with low phosphate concentrations, according to Santer, et al. (21), these results were not observed during this study.

Reactor (3), receiving the greatest influent phosphorous concentration (16.6 mg/l PO_4-P) did not show less polythionate accumulation than did Reactor (2), receiving a lesser amount of influent phosphorous (9.8 mg/l PO_4-P) and Reactor (1), which received the least influent phosphorous (3.0 mg/l PO_4-P).

Figure 11 indicates that from day five to day twenty, Reactor (1) recorded a consistently lower effluent polythionate concentration than did Reactors (2) and (3). For reactors (2) and

(3), results as to the effect of phosphorous on polythionate production are not conclusive, as the reactors interchanged positions of greatest effluent polythionate production.

From the results of this study, an influent phosphorous concentration of 3.0 mg/l PO_4-P produced the lowest effluent polythionate production. This result, however, is not considered to be general because of the trend of simultaneous rising and falling of effluent polythionate values, referred to earlier in section 5.1 of Chapter 5. This trend has been attributed to an inconsistent heating of the samples, with some samples receiving, possibly, a lesser degree of heating and others a greater degree.

The presence of polythionates in systems oxidizing thiosulphate and the effects of phosphorous on the production of polythionates has been noted by other experimenters.

Kreye, et al. (15) recorded a conversion of thiosulphate to tetrathionate, in one study, of better than 70 percent, when the influent phosphate concentration was 5.5 mg/l PO_4-P. In a second study, with an influent phosphate concentration of 14 mg/l PO_4-P, conversion of thiosulphate to tetrathionate decreased significantly, with a period of 15 days of no tetrathionate production. From this study of Kreye, larger values of influent phosphorous promoted more complete thiosulphate oxidation with periods of no intermediate tetrathionate production.

Graham (11) also reported formation of intermediate polythionates at an influent phosphate concentration of 60 mg/l PO_4 (19.5 mg/l PO_4-P). No attempt, however, was made to determine, specifically, what polythionates were produced.

BC Research (3), in studies on thiosulphate oxidation employing Rotating Biological Contactors, reported that with studies conducted at room temperature and 8.5°C, no tetrathionate or trithionate was detected with the qualitative analytical procedure used. Influent phosphate concentrations were 46 mg/l PO_4 (15mg/l PO_4-P) for both the room temperature and 8.5°C studies. For the 8.5°C study, influent phosphate was later reduced to 5 mg/l PO_4 (1.63 mg/l PO_4-P) and although the oxidation rate decreased no tetra - or trithionate was detected.

This result is in disagreement with Kreye, et al. (15), and supports the results obtained in this report.

The values of influent phosphorous concentrations did not appear to have a significant effect on the production of sulphate, the final oxidation state of thiosulphate. From Figure 20 the effluent sulphate concentrations for Reactors (1), (2) and (3) were, after the adjustments during day one to five, reasonably similar up to day fifteen, and for Reactors (1) and (2) reasonably similar up to day twenty, when monitoring was stopped.

It was noted earlier that polythionates accumulate in either the absence of phosphorous or with low phosphorous concentrations. This can also be interpreted as a decreased production of sulphate. For the three influent phosphorous concentrations used in this study, a decreased sulphate production was not noted between any of the reactors when they were functioning efficiently.

The measured production of effluent sulphate for all reactors on all days was greater than the value calculated theoretically from the overall thiosulphate oxidation equation, stated by Graham (11) as,

$$S_2O_3^{2-} + H_2O + 2O_2 \rightarrow 2SO_4^{2-} + 2H^+$$

which indicates that the complete oxidation of 1 gram of thiosulphate results in the production of 1.71 grams of sulphate.

It was expected that due to analytical erros the measured value of effluent sulphate would be less than the theoretical value. This was, however, not observed. The theoretical effluent sulphate concentration (i.e. 1546 mg/l) was always lower than the measured effluent sulphate concentration, with the exceptions occurring during the first few days of the study, when Reactors 1, 2 and 3 adjusted from batch to continuous flow operations, and the last days of Reactor (3), prior to its failure.

Tables 35 to 37 for Reactors 1, 2 and 3, respectively, summarize the measured and theoretical values of effluent sulphate production and show the lack of agreement between the measured effluent sulphate concentration and that obtained theoretically using the values of influent thiosulphate concentration (as determined by idiometric titration). This lack of agreement is attributed to errors in both the analytical procedures for the determination of influent thiosulphate and effluent sulphate.

There is better agreement, however, between the measured effluent sulphate concentration and that obtained using the theoretical influent thiosulphate concentration of 904 mg/l. This substantiates the assertion that the influent thiosulphate analysis could have been

TABLE 35.A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR REACTOR (1)

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	507.0	904	889.5	706.0	1546.0	1521.0	1333.0	1207.0
2	494.0	"	867.0	729.0	"	1483.0	1401.0	1247.0
3	519.0	"	911.0	694.0	"	1558.0	1633.0	1187.0
4	517.0	"	907.0	694.0	"	1551.0	1594.0	1187.0
5	528.0	"	926.0	694.0	"	1583.0	1620.0	1187.0
6	519.0	"	911.0	692.0	"	1558.0	1543.0	1183.0
7	514.0	"	902.0	688.0	"	1542.0	1646.0	1176.0
8	528.0	"	926.0	690.0	"	1583.0	1672.0	1180.0
9	514.0	"	902.0	692.0	"	1542.0	1724.0	1183.0
10	516.0	"	905.0	694.0	"	1548.0	1620.0	1187.0
11	520.0	"	912.0	688.0	"	1560.0	1672.0	1176.0
12	518.0	"	909.0	692.0	"	1554.0	1672.0	1183.0
13	525.5	"	922.0	690.0	"	1577.0	1672.0	1180.0
14	529.0	"	928.0	692.0	"	1587.0	1646.0	1183.0
15	525.0	"	922.0	688.0	"	1577.0	1698.0	1176.0
16	525.5	"	922.0	692.0	"	1577.0	1620.0	1183.0
17	523.5	"	918.0	692.0	"	1570.0	1646.0	1183.0
18	511.0	"	896.5	694.0	"	1533.0	1672.0	1187.0
19	508.0	"	891.0	692.0	"	1524.0	1672.0	1183.0
20	513.0	"	900.0	690.0	"	1539.0	1672.0	1180.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O$/l.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

TABLE 36. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR REACTOR (2)

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	514.0	904	902.0	706.0	1546.0	1542.0	1406.0	1207.0
2	496.0	"	870.0	706.0	"	1488.0	1437.0	1207.0
3	526.0	"	923.0	694.0	"	1578.0	1633.0	1187.0
4	524.5	"	920.0	694.0	"	1573.0	1594.0	1187.0
5	528.0	"	926.0	692.0	"	1583.0	1853.0	1183.0
6	526.0	"	923.0	692.0	"	1578.0	1569.0	1183.0
7	525.0	"	921.0	685.0	"	1575.0	1672.0	1171.0
8	521.0	"	914.0	681.0	"	1563.0	1672.0	1165.0
9	518.0	"	909.4	690.0	"	1554.0	1672.0	1180.0
10	512.0	"	898.0	674.0	"	1536.0	1620.0	1153.0
11	518.0	"	909.0	685.0	"	1554.0	1749.0	1171.0
12	520.0	"	912.0	690.0	"	1560.0	1672.0	1180.0
13	529.0	"	928.0	688.0	"	1587.0	1620.0	1176.0
14	521.5	"	915.0	694.0	"	1565.0	1749.0	1187.0
15	525.5	"	922.0	683.0	"	1577.0	1724.0	1168.0
16	525.5	"	922.0	681.0	"	1577.0	1646.0	1165.0
17	520.0	"	912.0	683.0	"	1560.0	1672.0	1168.0
18	525.0	"	921.0	683.0	"	1575.0	1672.0	1168.0
19	523.0	"	918.0	685.0	"	1570.0	1672.0	1171.0
20	517.0	"	907.0	692.0	"	1551.0	1672.0	1183.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O/l$.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

TABLE 37. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR REACTOR (3)

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	526.0	904.0	923.0	709.0	1546.0	1578.0	1168.0	1212.0
2	501.5	"	880.0	694.0	"	1505.0	1240.0	1187.0
3	524.5	"	920.0	692.0	"	1573.0	1550.0	1183.0
4	526.0	"	923.0	692.0	"	1578.0	1594.0	1183.0
5	496.0	"	870.0	687.0	"	1488.0	1569.0	1175.0
6	530.0	"	930.0	692.0	"	1590.0	1569.0	1183.0
7	524.0	"	919.0	690.0	"	1571.0	1646.0	1180.0
8	521.0	"	914.0	690.0	"	1563.0	1775.0	1180.0
9	518.0	"	909.0	692.0	"	1554.0	1724.0	1183.0
10	521.5	"	915.0	704.0	"	1565.0	1620.0	1204.0
11	520.5	"	912.0	683.0	"	1560.0	1724.0	1168.0
12	521.5	"	915.0	692.0	"	1565.0	1672.0	1183.0
13	521.5	"	915.0	697.0	"	1565.0	1646.0	1192.0
14	541.0	"	949.0	692.0	"	1623.0	1724.0	1183.0
15	525.5	"	922.0	690.0	"	1577.0	1724.0	1180.0
16	529.0	"	928.0	692.0	"	1587.0	1336.0	1183.0
17	535.0	"	939.0	697.0	"	1606.0	1155.0	1192.0
18	517.0	"	907.0	702.0	"	1551.0	1155.0	1200.0
19	523.0	"	917.0	695.0	"	1568.0	948.0	1188.0
20	519.0	"	910.0	695.0	"	1556.0	896.0	1188.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O$/l.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

in error, but now implies a decreased analytical error for effluent sulphate.

Also shown is the effluent sulphate concentration obtained from influent thiosulphate concentrations, which were, in turn, calculated theoretically from influent COD values, (using the stoichiometric relation for thiosulphate oxidation). The agreement with the measured effluent sulphate concentration is good.

Percentage conversion of thiosulphate to sulphate obtained by BC Research (3) varied from 85 to 95 percent. Polythionates were not detected, so the remaining percentage is not accounted for. LeClair (16) obtained percentage conversions which varied from 84 percent (at influent S_2O_3 concentration 6.61g/l and flow rate of 80 l/day) to 94 percent (at influent S_2O_3 concentration of 3.05 g/l and flow rate 160 l/day). LeClair attributes the presence of a small quantity of polythionates as responsible for the incomplete conversion.

6.1.1 Sulphur Balance

As an overall evaluation of thiosulphate oxidation, a sulphur balance was performed on the influent and effluent and is presented in Tables 38 to 40 for Reactors 1, 2 and 3, respectively.

Total influent sulphur was obtained from the addition of influent thiosulphate (as sulphur) and influent sulphate (as sulphur). Due to analytical errors in the determination of influent thiosulphate, using the idiometric procedure, influent COD values were therefore used to obtain influent thiosulphate concentrations using a stoichiometric relation for the chemical oxygen demand of thiosulphate. This relationship appears in section 6.1, and is repeated here as:

$$\text{mg/l } S_2O_3^{2-} = \text{mg/l COD}/0.57 \frac{\text{mgCOD}}{\text{mg } S_2O_3 2-}$$

Influent sulphate resulted, mainly, from the addition of the trace elements solution, the components of which were added as the metal sulphate, with one exception, $CaCl_2$.

Total effluent sulphur was obtained from the addition of effluent thiosulphate values (obtained from effluent COD values using the relationships noted above) and effluent sulphate values (obtained theoretically from the influent thiosulphate concentration which were obtained from influent COD values). The COD analysis was considered more reliable in obtaining the concentrations of influent thiosulphate oxidized to sulphate than the values of influent thiosulphate obtained analyticaly.

Measured effluent sulphate concentrations, using the titrametric

TABLE 38 SULPHUR BALANCE FOR REACTOR (I) PHOSPHOROUS VARIATION STUDY

AY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l)as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l)as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	507.0	889.5	507.0	60.0	20.0	527.0	42.5	75.0	42.5	51.0	29.0	1393	464	1521.0	507.0	549.5
2	494.0	867.0	494.0	60.0	20.0	514.0	27.0	47.0	27.0	59.0	34.0	1461	487	1483.0	494.0	521.0
3	519.0	911.0	519.0	60.0	20.0	539.0	28.0	49.0	28.0	62.0	35.0	1693	564	1558.0	519.0	547.0
4	517.0	907.0	517.0	60.0	20.0	537.0	27.0	47.0	27.0	44.0	25.0	1654	551	1551.0	517.0	544.0
5	528.0	926.0	528.0	60.0	20.0	548.0	32.0	56.0	32.0	22.0	12.5	1680	560	1583.0	528.0	560.0
6	519.0	911.0	519.0	60.0	20.0	539.0	44.0	77.0	44.0	26.0	15.0	1603	534	1558.0	519.0	563.0
7	514.0	902.0	514.0	60.0	20.0	534.0	38.0	67.0	38.0	61.0	35.0	1706	569	1542.0	514.0	552.0
8	528.0	926.0	528.0	60.0	20.0	548.0	37.0	65.0	37.0	43.0	24.5	1732	577	1583.0	528.0	565.0
9	514.0	902.0	514.0	60.0	20.0	534.0	31.5	55.0	31.5	30.0	17.0	1784	595	1542.0	514.0	545.5
10	516.0	905.0	516.0	60.0	20.0	536.0	35.0	61.0	35.0	36.0	20.5	1680	560	1548.0	516.0	551.0
11	520.0	912.0	520.0	60.0	20.0	540.0	29.5	52.0	29.5	30.0	17.0	1732	577	1560.0	520.0	549.5
12	518.0	909.0	518.0	60.0	20.0	538.0	24.0	42.0	24.0	27.0	15.0	1732	577	1554.0	518.0	542.0
13	525.5	922.0	525.5	60.0	20.0	545.5	31.5	55.0	31.5	22.0	12.5	1732	577	1577.0	526.0	557.5
14	529.0	928.0	529.0	60.0	20.0	549.0	26.0	46.0	26.0	36.5	21.0	1706	569	1587.0	529.0	555.0
15	525.5	922.0	525.5	60.0	20.0	545.5	24.0	42.0	24.0	22.0	12.5	1758	586	1577.0	526.0	550.0
16	525.5	922.0	525.5	60.0	20.0	545.5	24.0	42.0	24.0	23.0	13.0	1680	560	1577.0	526.0	550.0
17	523.5	918.0	523.5	60.0	20.0	543.5	28.0	49.0	28.0	22.0	12.5	1706	569	1570.0	523.0	551.0
18	511.0	896.5	511.0	60.0	20.0	531.0	26.0	46.0	26.0	26.0	15.0	1732	577	1533.0	511.0	537.0
19	508.0	891.0	508.0	60.0	20.0	528.0	34.0	60.0	34.0	35.0	20.0	1732	577	1524.0	508.0	542.0
20	513.0	900.0	513.0	60.0	20.0	533.0	34.0	60.0	34.0	19.0	11.0	1732	577	1539.0	513.0	547.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 39. SULPHUR BALANCE FOR REACTOR (2) PHOSPHOROUS VARIATION STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$ as $S_2O_3^{2-}$ (mg/l)	[1] Influent $S_2O_3^{2-}$ as S (mg/l)	Influent SO_4^{2-} as SO_4^{2-} (mg/l)	Influent SO_4^{2-} as S (mg/l)	[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$ as $S_2O_3^{2-}$ (mg/l)	[3] Effluent $S_2O_3^{2-}$ as S (mg/l)	[4] Effluent Polythionates as $S_2O_3^{2-}$ (mg/l)	[4] Effluent Polythionates as S (mg/l)	Measured Effluent SO_4^{2-} as SO_4^{2-} (mg/l)	Measured Effluent SO_4^{2-} as S (mg/l)	[5] Theoretical Effluent SO_4 as SO_4 (mg/l)	[5] Theoretical Effluent SO_4 as S (mg/l)	[6] Total Effluent Sulphur (mg/l) as S
1	514.0	902.0	514.0	60	20	534.0	58.5	103.0	58.5	93.0	53.0	1466	489	1542.0	514.0	572.5
2	496.0	870.0	496.0	60	20	516.0	53.0	93.0	53.0	37.0	21.0	1497	499	1488.0	496.0	549.0
3	526.0	923.0	526.0	60	20	546.0	25.0	44.0	25.0	57.0	32.5	1693	564	1578.0	526.0	551.0
4	524.5	920.0	524.5	60	20	544.5	23.0	40.0	23.0	41.0	23.0	1654	551	1573.0	524.0	547.0
5	528.0	926.0	528.0	60	20	548.0	34.0	60.0	34.0	28.0	16.0	1913	638	1583.0	528.0	562.0
6	526.0	923.0	526.0	60	20	546.0	44.0	77.0	44.0	43.0	24.5	1629	543	1578.0	526.0	570.0
7	525.0	921.0	525.0	60	20	545.0	40.0	70.0	40.0	78.0	44.5	1732	577	1575.0	525.0	565.0
8	521.0	914.0	521.0	60	20	541.0	41.0	72.0	41.0	62.0	35.0	1732	577	1563.0	521.0	562.0
9	518.0	909.0	518.0	60	20	538.0	37.0	65.0	37.0	38.0	22.0	1732	577	1554.0	518.0	555.0
10	512.0	898.0	512.0	60	20	532.0	35.0	61.0	35.0	46.0	26.0	1680	560	1536.0	512.0	547.0
11	518.0	909.0	518.0	60	20	538.0	35.0	61.0	35.0	41.0	23.0	1809	603	1554.0	518.0	553.0
12	520.0	912.0	520.0	60	20	540.0	33.5	59.0	33.5	43.0	24.5	1732	577	1560.0	520.0	553.5
13	529.0	928.0	529.0	60	20	549.0	39.0	68.0	39.0	46.0	26.0	1680	560	1587.0	529.0	568.0
14	521.5	915.0	521.5	60	20	541.5	41.0	72.0	41.0	42.0	24.0	1809	603	1565.0	522.0	563.0
15	525.5	922.0	525.5	60	20	545.5	35.0	61.0	35.0	33.0	19.0	1784	595	1577.0	526.0	561.0
16	525.5	922.0	525.5	60	20	545.5	35.0	61.0	35.0	42.0	24.0	1706	569	1577.0	526.0	561.0
17	520.0	912.0	520.0	60	20	540.0	35.0	61.0	35.0	42.0	24.0	1732	577	1560.0	520.0	555.0
18	525.0	921.0	525.0	60	20	545.0	28.0	49.0	28.0	48.0	27.0	1732	577	1575.0	525.0	553.0
19	523.0	918.0	523.0	60	20	543.0	34.0	60.0	34.0	46.0	26.0	1732	577	1570.0	523.0	557.0
20	517.0	907.0	517.0	60	20	537.0	36.0	63.0	36.0	34.0	19.0	1732	577	1551.0	517.0	553.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the Influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 40. SULPHUR BALANCE FOR REACTOR (3) PHOSPHOROUS VARIATION STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	526.0	923.0	526.0	60	20	546.0	81.5	143.0	81.5	80.0	46.0	1228	409.0	1578.0	526.0	607.5
2	501.5	880.0	501.5	60	20	521.5	41.0	72.0	41.0	46.0	26.0	1300	433.0	1505.0	502.0	543.0
3	524.5	920.0	524.5	60	20	544.5	23.0	40.0	23.0	52.0	35.0	1610	537.0	1573.0	524.0	547.0
4	526.0	923.0	526.0	60	20	546.0	25.0	44.0	25.0	34.0	19.0	1654	551.0	1578.0	526.0	551.0
5	496.0	870.0	496.0	60	20	516.0	32.0	56.0	32.0	36.5	21.0	1629	543.0	1488.0	496.0	528.0
6	530.0	930.0	530.0	60	20	550.0	35.0	61.0	35.0	41.0	23.0	1629	543.0	1590.0	530.0	565.0
7	524.0	919.0	524.0	60	20	544.0	30.0	53.0	30.0	61.0	35.0	1706	569.0	1571.0	524.0	554.0
8	521.0	914.0	521.0	60	20	541.0	35.0	61.0	35.0	71.0	40.5	1835	612.0	1563.0	521.0	556.0
9	518.0	909.0	518.0	60	20	538.0	31.5	55.0	31.5	41.0	23.0	1784	595.0	1554.0	518.0	549.5
10	521.5	915.0	521.5	60	20	541.5	26.0	46.0	26.0	45.5	26.0	1680	560.0	1565.0	522.0	548.0
11	520.0	912.0	520.0	60	20	540.0	28.0	49.0	28.0	54.0	31.0	1784	595.0	1560.0	520.0	548.0
12	521.5	915.0	521.5	60	20	541.5	20.0	35.0	20.0	48.0	27.0	1732	577.0	1565.0	522.0	542.0
13	521.5	915.0	521.5	60	20	541.5	31.5	55.0	31.5	44.0	25.0	1706	569.0	1565.0	522.0	553.5
14	541.0	949.0	541.0	60	20	561.0	29.5	52.0	29.5	47.0	27.0	1784	595.0	1623.0	541.0	570.5
15	525.5	922.0	525.5	60	20	545.5	22.0	39.0	22.0	56.0	32.0	1784	595.0	1577.0	526.0	548.0
16	529.0	928.0	529.0	60	20	549.0	108.0	189.0	108.0	235.0	157.0	1396	465.0	1587.0	529.0	637.0
17	535.0	939.0	535.0	60	20	555.0	160.0	281.0	160.0	299.0	170.0	1215	405.0	1606.0	535.0	695.0
18	517.0	907.0	517.0	60	20	537.0	169.0	296.5	169.0	341.0	194.0	1215	405.0	1551.0	517.0	711.0
19	523.0	917.0	523.0	60	20	543.0	209.0	367.0	209.0	375.0	214.0	1008	336.0	1568.0	527.0	726.0
20	519.0	910.0	519.0	60	20	539.0	224.0	393.0	224.0	404.0	230.0	956	319.0	1556.0	519.0	743.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the Influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

procedure outlined in Chapter 4, were consistently greater (by about 100 to 150 mg/l) than the theoretical effluent sulphate concentrations, at all times except during day one and two for Reactors 1, 2 and 3. Analytical errors were considered responsible, but it is noted that the difference was fairly constant.

A comparison of the values of Total influent sulphur and Total effluent sulphur for all Reactors, shows good agreement, with Total effluent sulphur consistently greater by amounts varying, approximately, from 4 to 50 mg/l. The comparisons for the last five days of Reactor 3 (i.e.,days 15 to 20) are not considered valid as the reactor had failed.

If measured effluent sulphate values were used in place of the theoretical effluent sulphate, then the Total effluent sulphur values would be slightly greater and thus the agreement with Total influent sulphur not as good. It is thought that analytical errors were responsible for the higher measured effluent sulphate values, as compared to the theoretical effluent sulphate, and thus they were not used in the computation for Total effluent sulphur.

6.2 Retention Time Variation Study

Results of the 4,3,2,1 and ½ day retention time studies, in some areas, are reasonably similar with each other and similar also to the results of the phosphorous variation study. Much of the discussion, therefore, relating to the results of the phosphorous variation study is applicable to the results of the retention time studies.

Influent pH values were similar for the duration of the 4 and 3 day retention time studies. For the 2 and 1 day retention time studies, influent pH values were similar to each other, and slightly greater than those for the 4 and 3 day retention time studies, but not significantly so. The ½ day retention time study recorded, in most cases, the highest influent pH values.

Mixed Liquor and effluent pH values were constant for the 4,3,2 and 1 day retention time studies, at pH 2.10. For the ½ day retention time study, after the "shock effect" on day one, brought about by changing the retention time from a previous value (see Table 26), when mixed liquor and effluent pH was 2.55, the pH values were the same as for the other retention times.

Thus, retention time seems to have little effect upon mixed liquor and effluent pH, even though the influent pH varied slightly among the different retention times. Down to ½ day retention time, mixed liquor and effluent pH values were pH 2.10 up to reactor failure.

At the onset of reactor failure, for the ½ day retention time, the mixed liquor pH increased slowly from pH 2.25 (day 10) to pH 2.60 (day 11) and then dramatically to pH 6.30 (day 12). This dramatic increase is thought to be due to the flow rate of 10 l/day, required for a retention time for ½ day. Where at lower influent flow rates the pH would have increased gradually, with a large flow rate. The assimilative i.e. oxidative, capacity of the mixed liquor is reduced and pH increase is determined largely by the influent flowrate at a near nuetral pH.

At ¼ day retention time, similar conditions were observed when, with an influent flow rate of 20 l/day, in a matter of 5 minutes after starting pumping at this value of 20 l /day, the mixed liquor pH increased from pH 2.1 to 2.3. On the next morning at 11:00 am, after approximately 16 hours of pumping, the mixed liquor pH was 7.3, the same as the influent, and had the consistency and appearance of the influent (that is, an appearance similar to tap water - colourless and transparent). Thus, based solely on the mixed liquor and effluent pH values, the washout retention time, at room temperatures, is between ¼ and ½ day.

MLTSS and MLVSS values for each retention time study, as for the phosphorous variation study, showed great variation from day to day despite a sample volume of 250 ml used to obtain these values. This shows that even relatively large volumes, as compared to the 25 ml volumes used in the phosphorous variation study, do not give reliable results. The reason advanced for this variation is the presence of a colloidal suspension, possibly of elemental sulphur, in the reactor, which would interfere with the TSS and VSS analyses.

Comparing MLTSS and MLVSS values at the different retention times shows that for the 4, 3 and 2 day retention times, values were similar and slightly greater than the values for the 1 and ½ day retention times. MLTSS and MLVSS values for the 1 and ½ day retention time studies were similar to each other.

These results show that retention times of from 4 to 2 days have little effect on either MLTSS or MLVSS values, although this could be due to the lack of sensitivity of the analytical procedure at low TSS and VSS concentrations. A better estimation of VSS, such as organic carbon or organic nitrogen would confirm this.

The slightly lower VSS values for the 1 and ½ day retention time studies as compared to the 4, 3 and 2 day retention times, agree with the principles of bacterial growth in continuous flow systems which stipulates a sufficient retention time for reproduction. However, for the 1 day and ½ day retention time studies, the day one values of TSS and VSS were larger than the values recorded for the remainder of the respective studies. (The TSS and VSS values were 10 mg/1 and 10mg/1, respectively, for the 1 day retention time, and 30 mg/1 and 29 mg/1, respectively, for the ½ day retention time. This increase in VSS on day one at both these retention times is of particular note, as when the retention time decreases, the VSS values should not increase because wash out conditions are approached and bacterial reproduction is affected.

This increase is attributed to the "shock effect" mentioned earlier. See Table 26.

For the ½ day retention time, on day ten where reactor failure starts the TSS and VSS values are identical at 16.8 mg/1 clearly in disagreement with the principles of bacterial growth.

This again shows the imprecision of the VSS test as an indicator of biomass.

Effluent turbidity values proved more consistent, on a day to day basis, than did the TSS and VSS values. Section 5.2 of Chapter 5, contains much of the discussion on effluent turbidity values.

As there is very little explicit reference to effluent turbidity values and retention times in the literature, a comparison with other work is, therefore, unavailable.

Of note, however, is the sudden increase in turbidity which preceeds reactor failure. This is particularly apparent with the ½ day retention time study. On day nine of this study effluent turbidity, was 22 NTU, which by day ten had increased to 120 NTU. This turbidity increase was accompanied by a rise in MLTSS and a rise in mixed liquor and effluent pH values from 2.10 to 2.25.

For the ¼ day retention time study, a turbidity increase was also noted but was more apparent, occuring over a shorter time interval. Mixed liquor turbidity increased visually in the space of about 5 minutes after pumping was started at the flow rate of 20 l/day, necessary for a ¼ day retention time. On the next morning at 11:00 AM., after approximately 16 hours of influent flow, the mixed liquor was no longer as turbid as it has been before the start of influent pumping, and had the appearance of tap water, i.e., colourless and transparent. The same increase in turbidity, prior to reactor failure, was also noted in the phosphorous variation study for Reactor (3).

Apparently, then, turbidity can be used as an indicator of reactor performance and efficiency as reactor failure was always preceeded by a rapid rise in effluent turbidity values.

The effect of retention times on COD removals, from the results, is apparent only below a retention time of 2 days. The 4, 3 and 2 day retention times exhibited COD removals greater than 90 percent, whereas for the 1 and ½ day retention times COD removals decreased and were always below 90 percent, except on two occasions, but greater than 80 percent. Thus, there was a definite decrease in reactor performance, with respect to COD removal, at retention times less than 2 days.

Increases in effluent COD and decreases in COD removal on day one of the ½ day retention time study are due to the "shock effect" resulting in a change of retention time from the previous retention time study. See Table 26. At the ½ day retention time some recovery was made from the day one value of effluent COD but on subsequent days effluent COD values were greater than those of the 4, 3 and 2 day retention times.

By contrast, effluent thiosulphate concentrations remained constant at 3.0 mg/l throughout the retention time studies, except for day one of both the 1 and ½ day retention times. These increase are due, again, to the "shock effect". See Table 26. Although effluent thiosulphate for the ½ day retention time study increased to 6.0 mg/l on day one, by day two it had recovered to 3.0 mg/l. However, this retention time wasn't sufficient to allow a complete recovery, and operation at this retention times would, it is thought, be susceptible to any stress.

Thus, retention times of 4, 3, 2 and 1 day had little effect on Thiosulphate removal, but a retention time of ½ day resulted ultimately in reactor failure. At this value of retention time (i.e. ½ day) the reactor might not be washed out but extremely sensitive to operational changes.

It should be noted, also, that effluent thiosulphate concentration together with the effluent polythionate concentration were not in agreement with the effluent COD concentrations when the COD values were translated to the stoichiometric equivalent thiosulphate concentration. This lack of agreement was noted for the duration of all the retention time studies, and is attributed to analytical errors for both effluent thiosulphate and polythionate determination.

Effluent polythionate concentrations for the retention time studies are outlined in Chapter 5, section 5.2.

The effect of different retention times is not conclusive as it is thought that non-uniform or inconsistent heating, as explained in Chapter 5, section 5.2, resulted in low polythionate concentrations at the lower retention times.

An alternate explanation for the decrease in polythionates at these lower retention times could be in the work of Parker and Prisk (20). According to Parker and Prisk, microbiological studies with Thiobacillus thiooxidans, indicate the formation of polythionates and their eventual oxidation as being time dependent. Thus, at lower retention times, polythionates concentrations should be, accordingly, lower. It should also be noted that at too low a value of retention time, polythionates will not be allowed to form and washout conditions may prevail.

The ability to assess polythionate formation at lower retention times, however, depends on the accuracy of the analytical method used. It is believed that the titrametric procedure used in this report for polythionate determination was susceptible to error.

The literature, unfortunately, does not refer specifically to polythionate formation, but only to the overall thiosulphate removal or thiosulphate oxidation rates, at various retention times. Thus, polythionate concentrations must be inferred when noting overall thiosulphate removal rates and other effluent characteristics.

The production of sulphate did not appear to be significantly affected by different retention times.

Although effluent sulphate concentration decreased on day one of the ½ day retention time study to 1310 mg/l, by day two the unit had recovered, with the sulphate concentration at 1698 mg/l. Impending reactor failure is noted on day ten of the ½ day retention time study with a decrease in effluent sulphate concentration.

Measured effluent sulphate concentrations were, as for the phosphorous variation study, greater than the theoretical effluent sulphate concentration, as calculated from the measured influent thiosulphate values. This is probably due to analytical errors in the determination of influent thiosulphate concentration and possible oxidation of influent thiosulphate to polythionates. As no polythionate analysis was conducted on the influent, this claim cannot be substantiated.

Agreement, however, between the theoretical effluent sulphate concentration computer from the theoretical influent thiosulphate concentration (which was obtained from influent COD values, considered to be more reliable than the measured influent thiosulphate concentrations) and the measured effluent sulphate concentration was good, with a percentage error in the neighbourhood of ± 10%. This error is within the analytical limitations of the sulphate analysis.

Tables 41 to 45 , for the 4,3,2,1 and ½ day retention time studies, respectively, summarize the measured and theoretical values of effluent sulphate concentrations.

Overall, the results of this study indicate that a retention time of 1 day at room temperatures is the minimum value of retention time required for satisfactory thiosulphate oxidation.

Other investigations conducted into the effects of different retention times on thiosulphate oxidation indicate that the growth system used, whether suspended growth (completely mixed reactors with and without recycle) or fixed film reactors (Rotating Biological Contactors or "Biodiscs"), determines the minimum retention times capable of satisfactory thiosulphate oxidation. In general, fixed film reactors, with their larger biomass concentrations are capable of operating at lower retention times than suspended growth reactors.

Of the fixed film reactor studies, Lockett (18) reported that a 910 mg/l thiosulphate solution was "completely oxidized in 5 contacts", each contact lasting 2 hours. BC Research (3) reported that, at room temperature a retention time of 34 minutes reduced the thiosulphate concentration from 960 mg/l (influent) to 25 mg/l (effluent)

TABLE 41. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR 4 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical^1	From Influent COD^2	Measured^3	Theoretical^4	From Influent COD^5	Measured^6	Theoretical^7
1	539.0	904.0	946.0	692.0	1546.0	1618.0	1672.0	1183.0
2	539.0	"	946.0	702.0	"	1618.0	1698.0	1200.0
3	539.0	"	946.0	695.0	"	1618.0	1672.0	1188.0
4	541.0	"	949.0	699.0	"	1623.0	1672.0	1195.0
5	535.0	"	939.0	681.0	"	1606.0	1620.0	1165.0
6	550.0	"	965.0	697.0	"	1650.0	1672.0	1192.0
7	537.0	"	942.0	692.0	"	1611.0	1698.0	1183.0
8	502.0	"	881.0	694.0	"	1507.0	1698.0	1187.0
9	508.0	"	891.0	692.0	"	1524.0	1672.0	1183.0
10	502.0	"	881.0	694.0	"	1507.0	1672.0	1187.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O/l$.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

TABLE 42.A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR 3 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	537.0	904.0	942.0	685.0	1546.0	1611.0	1646.0	1171.0
2	537.0	"	942.0	695.0	"	1611.0	1620.0	1188.0
3	537.0	"	942.0	695.0	"	1611.0	1672.0	1188.0
4	537.0	"	942.0	692.0	"	1611.0	1672.0	1183.0
5	537.0	"	942.0	695.0	"	1611.0	1672.0	1188.0
6	547.0	"	960.0	688.0	"	1642.0	1672.0	1176.0
7	537.0	"	942.0	692.0	"	1611.0	1672.0	1183.0
8	502.0	"	881.0	699.0	"	1507.0	1672.0	1195.0
9	508.0	"	891.0	694.0	"	1524.0	1672.0	1187.0
10	506.0	"	888.0	694.0	"	1518.0	1724.0	1187.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O/l$.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

TABLE 43. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR 2 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	525.0	904.0	921.0	692.0	1546.0	1575.0	1646.0	1183.0
2	552.0	"	968.0	692.0	"	1655.0	1672.0	1183.0
3	537.0	"	942.0	692.0	"	1611.0	1672.0	1183.0
4	504.0	"	884.0	692.0	"	1512.0	1698.0	1183.0
5	485.0	"	851.0	692.0	"	1455.0	1724.0	1183.0
6	498.0	"	874.0	694.0	"	1495.0	1724.0	1187.0
7	521.0	"	914.0	704.0	"	1563.0	1672.0	1204.0
8	515.5	"	904.0	692.0	"	1546.0	1646.0	1183.0
9	515.5	"	904.0	702.0	"	1546.0	1672.0	1200.0
10	519.0	"	910.0	711.0	"	1556.0	1672.0	1216.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O/l$.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

TABLE 44. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR 1 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	521.0	904.0	914.0	692.0	1546.0	1563.0	1672.0	1183.0
2	517.5	"	908.0	702.0	"	1553.0	1672.0	1200.0
3	446.0	"	782.0	650.0	"	1337.0	1672.0	1112.0
4	448.0	"	786.0	699.0	"	1344.0	1672.0	1195.0
5	513.0	"	900.0	702.0	"	1539.0	1620.0	1200.0
6	507.0	"	889.5	692.0	"	1521.0	1672.0	1183.0
7	477.0	"	837.0	664.0	"	1431.0	1698.0	1135.0
8	488.0	"	856.0	660.0	"	1464.0	1646.0	1129.0
9	485.5	"	852.0	657.0	"	1457.0	1672.0	1123.0
10	462.0	"	810.5	629.0	"	1386.0	1620.0	1076.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O/l$.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x Influent thiosulphate).

TABLE 45. A COMPARISON OF ACTUAL AND THEORETICAL VALUES OF EFFLUENT SULPHATE PRODUCTION FOR ½ DAY RETENTION TIME STUDY.

DAY	Influent COD (mg/l)	Influent Thiosulphate (mg/l)			Effluent Sulphate (mg/l)			
		Theoretical[1]	From Influent COD[2]	Measured[3]	Theoretical[4]	From Influent COD[5]	Measured[6]	Theoretical[7]
1	512.0	904.0	898.0	699.0	1546.0	1536.0	1310.0	1195.0
2	518.5	"	910.0	718.0	"	1556.0	1698.0	1228.0
3	518.5	"	910.0	695.0	"	1556.0	1672.0	1188.0
4	522.0	"	916.0	713.0	"	1566.0	1646.0	1219.9
5	522.0	"	916.0	695.0	"	1566.0	1672.0	1188.0
6	499.0	"	875.0	692.0	"	1496.0	1698.0	1183.0
7	495.0	"	868.0	678.0	"	1484.0	1672.0	1159.0
8	503.0	"	882.0	685.0	"	1508.0	1620.0	1171.0
9	485.5	"	852.0	650.0	"	1457.0	1620.0	1112.0
10	493.0	"	865.0	664.0	"	1479.0	1568.0	1135.0

[1] Calculated theoretically from the influent thiosulphate concentration of 2000 mg $Na_2S_2O_3.5H_2O$/l.

[2] Calculated from influent COD values as (COD/0.57).

[3] Observed by idiometric titration for thiosulphate.

[4] Calculated theoretically from the influent thiosulphate concentration as (1.71 x 904 mg/l).

[5] Calculated from the influent thiosulphate concentration (from influent COD) as (1.71 x influent thiosulphate).

[6] Observed by titration for sulphate analysis.

[7] Calculated theoretically from the measured influent thiosulphate concentration as (1.71 x influent thiosulphate).

with a thiosulphate oxidation rate of 208 mg/ft^2/hr. A retention time of 60 minutes reduced the thiosulphate concentration from 1050 mg/l (influent) to less than 10 mg/l (effluent), with a thiosulphate oxidation rate of 222 mg/ft^2/hr. Thus, for this study with fixed film reactors, nearly doubling the retention time had little effect on thiosulphate oxidation rates. LeClair (16) reported a retention time of 2.2 hours as being sufficient to reduce an influent containing 950 mg/l thiosulphate by 87 percent.

Of the suspended growth reactor studies, Schmidt (22) reported a retention time of 48 hours (2 days) at room temperature as reducing the influent thiosulphate concentration from 1000 mg/l to 0 mg/l in the effluent. A similar reduction was obtained with a retention time of 18 hours, also at room temperature. Schmidt also obtained a minimum retention time of 6 hours (¼ day) which was sufficient to reduce an influent thiosulphate concentration from 400 mg/l to 40 mg/l in the effluent, a 90 percent removal.

This result of Schmidt's stands in contrast with the results obtained at a ¼ day retention time in this report. Immediate reactor failure was reported at a retention time of ¼ day. However, as the influent thiosulphate concentration was greater than the 400 mg/l used by Schmidt, this could be a possible explanation for reactor failure at the retention time of ¼ day.

6.2.1 Sulphur Balance

Tables 46 to 50 summarize sulphur balances for the 4, 3, 2, 1 and ½ day retention time studies, respectively.

A discussion on the nature of the individual components of total influent sulphur and total effluent sulphur and the reasons for their inclusion has been made earlier in Section 6.1.1 and reference is made to that section.

A comparison of the values of total influent sulphur and total effluent sulphur shows good agreement, with total effluent sulphur consistently greater by amounts of, approximately, 25 mg/l sulphur for the five retention times. For the 1 and ½ day Retention Time studies, however, there were two occasions when a larger disagreement, of up to about 45 mg/l was noted. In general, though, the agreement was good.

TABLE 46-SULPHUR BALANCE FOR THE 4 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	539.0	946.0	539.0	60	20	559.0	43.0	75.0	43.0	4.5	3.0	1732	577	1618.0	539.0	582.0
2	539.0	946.0	539.0	60	20	559.0	46.5	82.0	46.5	33.0	19.0	1758	586	1618.0	539.0	585.5
3	539.0	946.0	539.0	60	20	559.0	46.5	82.0	46.5	16.0	9.0	1732	577	1618.0	539.0	585.5
4	541.0	949.0	541.0	60	20	561.0	43.0	75.0	43.0	31.0	18.0	1732	577	1623.0	541.0	584.0
5	535.0	939.0	535.0	60	20	555.0	43.0	75.0	43.0	38.0	22.0	1680	560	1606.0	535.0	578.0
6	550.0	965.0	550.0	60	20	570.0	48.5	85.0	48.5	9.0	5.0	1732	577	1650.0	550.0	598.5
7	537.0	942.0	537.0	60	20	557.0	35.0	61.0	35.0	28.0	16.0	1758	586	1611.0	537.0	572.0
8	502.0	881.0	502.0	60	20	522.0	41.0	72.0	41.0	27.0	15.0	1758	586	1507.0	502.0	543.0
9	508.0	891.0	508.0	60	20	528.0	45.0	79.0	45.0	22.0	12.5	1732	577	1524.0	508.0	553.0
10	502.0	881.0	502.0	60	20	522.0	43.0	75.0	43.0	32.0	18.0	1732	577	1507.0	502.0	545.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 47. SULPHUR BALANCE FOR THE 3 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	537.0	942.0	537.0	60	20	557.0	41.0	72.0	41.0	17.0	10.0	1706	569.0	1611.0	537.0	578.0
2	537.0	942.0	537.0	60	20	557.0	37.0	65.0	37.0	34.0	19.0	1680	560.0	1611.0	537.0	574.0
3	537.0	942.0	537.0	60	20	557.0	33.0	58.0	33.0	38.0	22.0	1732	577.0	1611.0	537.0	570.0
4	537.0	942.0	537.0	60	20	557.0	29.0	51.0	29.0	34.0	19.0	1732	577.0	1611.0	537.0	566.0
5	537.0	942.0	537.0	60	20	557.0	25.0	44.0	25.0	29.0	16.5	1732	577.0	1611.0	537.0	562.0
6	547.0	960.0	547.0	60	20	567.0	27.0	47.0	27.0	34.0	19.0	1732	577.0	1642.0	547.0	574.0
7	537.0	942.0	537.0	60	20	557.0	23.0	40.0	23.0	28.0	16.0	1732	577.0	1611.0	537.0	560.0
8	502.0	881.0	502.0	60	20	522.0	35.0	61.0	35.0	34.0	19.0	1732	577.0	1507.0	502.0	537.0
9	508.0	891.0	508.0	60	20	528.0	31.0	54.0	31.0	31.0	18.0	1732	577.0	1524.0	508.0	539.0
10	506.0	888.0	506.0	60	20	526.0	31.0	54.0	31.0	33.0	19.0	1784	595.0	1518.0	506.0	537.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the Influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 4B, SULPHUR BALANCE FOR THE 2 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	525.0	921.0	525.0	60	20	545.0	37.0	65.0	37.0	33.0	19.0	1706	569.0	1575.0	525.0	562.0
2	552.0	968.0	552.0	60	20	572.0	46.5	82.0	46.5	34.0	19.0	1732	577.0	1655.0	552.0	598.5
3	537.0	942.0	537.0	60	20	557.0	39.0	68.0	39.0	27.0	15.0	1732	577.0	1611.0	537.0	576.0
4	504.0	884.0	504.0	60	20	524.0	43.0	75.0	43.0	33.0	19.0	1758	586.0	1512.0	504.0	547.0
5	485.0	851.0	485.0	60	20	505.0	43.0	75.0	43.0	35.0	20.0	1784	595.0	1455.0	485.0	528.0
6	498.0	874.0	498.0	60	20	518.0	45.0	79.0	45.0	33.0	19.0	1784	595.0	1495.0	498.0	543.0
7	521.0	914.0	521.0	60	20	541.0	43.0	75.0	43.0	21.0	12.0	1732	577.0	1563.0	521.0	564.0
8	515.5	904.0	515.5	60	20	535.5	31.0	54.0	31.0	29.0	16.5	1706	569.0	1546.0	515.0	546.0
9	515.5	904.0	515.5	60	20	535.5	27.0	47.0	27.0	34.0	19.0	1732	577.0	1546.0	515.0	542.0
10	519.0	910.0	519.0	60	20	539.0	31.0	54.0	31.0	31.0	18.0	1732	577.0	1556.0	519.0	550.0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 49. SULPHUR BALANCE FOR THE 1 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	[1] Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3] Effluent $S_2O_3^{2-}$		[4] Effluent Polythionates		Measured Effluent SO_4^{2-}		[5] Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	521.0	914.0	521.0	60	20	541.0	37.0	65.0	37.0	9.0	5.0	1732	577.0	1563.0	521.0	558.0
2	517.5	908.0	517.5	60	20	537.5	43.0	75.0	43.0	29.0	16.5	1732	577.0	1553.0	518.0	561.0
3	446.0	782.0	446.0	60	20	466.0	61.0	107.0	61.0	29.0	16.5	17[illegible]	577.0	1337.0	446.0	507.0
4	448.0	786.0	448.0	60	20	468.0	69.0	121.0	69.0	32.0	18.0	17[illegible]	577.0	1344.0	448.0	517.0
5	513.0	900.0	513.0	60	20	533.0	67.0	117.5	67.0	22.0	12.5	1680	560.0	1539.0	513.0	580.0
6	507.0	889.5	507.0	60	20	527.0	61.0	107.0	61.0	26.0	15.0	1732	577.0	1521.0	507.0	567.0
7	477.0	837.0	477.0	60	20	497.0	53.0	93.0	53.0	27.0	15.0	1758	586.0	1431.0	477.0	530.0
8	488.0	856.0	488.0	60	20	508.0	56.0	98.0	56.0	28.0	16.0	1706	569.0	1464.0	488.0	544.0
9	485.5	852.0	485.5	60	20	505.5	58.5	102.0	58.0	25.0	14.0	1732	577.0	1457.0	486.0	544.0
10	462.0	810.5	462.0	60	20	482.0	49.0	86.0	49.0	30.0	17.0	1680	560.0	1386.0	462.0	51[illegible].0

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the Influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

TABLE 50. SULPHUR BALANCE FOR THE 3 DAY RETENTION TIME STUDY

DAY	Influent COD (mg/l)	[1]Influent $S_2O_3^{2-}$		Influent SO_4^{2-}		[2] Total Influent Sulphur (mg/l) as S	Effluent COD (mg/l)	[3]Effluent $S_2O_3^{2-}$		[4]Effluent Polythionates		Measured Effluent SO_4^{2-}		[5]Theoretical Effluent SO_4		[6] Total Effluent Sulphur (mg/l) as S
		as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)			as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as $S_2O_3^{2-}$ (mg/l)	as S (mg/l)	as SO_4^{2-} (mg/l)	as S (mg/l)	as SO_4 (mg/l)	as S (mg/l)	
1	512.0	898.0	512.0	60	20	532.0	70.0	123.0	70.0	153.5	87.5	1370	457.0	1536.0	512.0	592.0
2	518.5	910.0	518.5	60	20	538.5	67.0	117.5	67.0	27.0	15.0	1758	586.0	1556.0	519.0	586.0
3	518.5	910.0	518.5	60	20	538.5	65.0	114.0	65.0	18.0	10.0	1732	577.0	1556.0	519.0	584.0
4	522.0	916.0	522.0	60	20	542.0	67.0	117.5	67.0	21.0	12.0	1706	569.0	1566.0	522.0	589.0
5	522.0	916.0	522.0	60	20	542.0	63.0	110.5	63.0	23.0	13.0	1732	577.0	1566.0	522.0	585.0
6	499.0	875.0	499.0	60	20	519.0	57.0	100.0	57.0	24.0	14.0	1758	586.0	1496.0	499.0	556.0
7	495.0	868.0	495.0	60	20	515.0	64.0	112.0	64.0	26.0	15.0	1732	577.0	1484.0	495.0	559.0
8	503.0	882.0	503.0	60	20	523.0	54.0	95.0	54.0	25.0	14.0	1680	560.0	1508.0	503.0	557.0
9	485.5	852.0	485.5	60	20	505.0	50.5	89.0	50.5	51.0	29.0	1680	560.0	1457.0	486.0	536.5
10	493.0	865.0	493.0	60	20	513.0	50.5	89.0	50.5	42.0	24.0	1628	543.0	1479.0	493.0	543.5

[1] Calculated theoretically from Influent COD values as (COD/0.57).

[2] Obtained from the addition of Influent $S_2O_3^{2-}$ and Influent SO_4^{2-}, both as (mg/l) S.

[3] Calculated theoretically from Effluent COD values as (COD/0.57).

[4] Assumed to be as $S_2O_3^{2-}$ only.

[5] Calculated theoretically from the Influent thiosulphate concentration (from Influent COD values).

[6] Obtained from the addition of Effluent $S_2O_3^{2-}$ (from effluent COD) and Theoretical Effluent SO_4^{2-}.

6.3 The Mechanism of Thiosulphate Oxidation

It was assumed throughout both the phosphorous variation and retention time studies, that the oxidation of thiosulphate to sulphate proceeded biologically. That is, the utilization of thiosulphate by Thiobacillus thiooxidans, which was added to the mixed liquor during the acclimatization process, and the subsequent conversion, i.e. oxidation, to sulphate, was the sole operating mechanism. Possible oxidation of thiosulphate by air from the diffused air stones was thought to have been negligible.

However, Uko (27), reporting on the precipitation of sulphur from solutions containing thiosulphate as a treatment process for the removal of thiosulphate from mill waste waters, challenges this assumption by noting studies which indicated that at pH values below 5.0, thiosulphate dissociates to sulphite (SO_3^{2-}) and elemental sulphur (S^o):

$$S_2O_3^{2-} \longrightarrow SO_3^{2-} + S^o \qquad \text{(slow)} \;..... \qquad (25)$$

This reaction can be strongly catalyzed by the presence of copper in solution.

Sulphite is then rapidly oxidized by oxygen to form sulphate:

$$SO_3^{2-} + \tfrac{1}{2}O_2 \longrightarrow SO_4^{2-} \qquad \text{(fast)} \;..... \qquad (26)$$

Sinha and Walden (24) also report thiosulphate dissociation at pH values below 4.0. Thiosulphate concentration, however, is not stated.

To investigate the above result, a 2000 mg/l solution of thiosulphate (as $Na_2S_2O_3.5H_2O$) was acidified by the addition of 1N HNO_3.

Thiosulphate dissociation at this concentration, identical to the concentrations used for both studies constituting this report, was found to occur only below pH 3.0, although the time allowed at pH 3.0 may not have been enough. Table 51 summarizes the results.

TABLE 51

ONSET OF TURBIDITY WITH ACIDIFICATION OF
A THIOSULPHATE SOLUTION

Initial pH	Final pH	Onset of Turbidity*
8.10	3.0	5 minutes after pH change - no turbidity
3.0	2.0	2 minutes after pH change - slight turbidity
		5 minutes after pH change - more turbidity than at 2 min.
		10 minutes after pH change - turbidity greater than at 5 min.

* Visual estimation only.

When the acidified thiosulphate solution at pH 2.0 was passed through a 45 micron filter, a yellow residue on the filter was observed. No qualitative tests were performed to determine whether the residue was elemental sulphur. The appearance, however, suggested so.

Thus the possibility exists that at the mixed liquor pH values of 2.10, thiosulphate dissociation to SO_3^{2-} and S^o could have occurred. Furthermore, the air supply from the air stone could have been sufficient to facilitate the oxidation of SO_3^{2-} to SO_4^{2-}. The elemental sulphur produced, which could have accounted for the turbidity and inconsistent TSS and VSS values, would not have been oxidized to sulphate by the air supply, but could have been oxidized to sulphate by the presence of T. thiooxidans. According to Scott and Bragg (23) and Trudinger (26), these bacteria can utilize elemental sulphur in place of thiosulphate thus obtaining the energy for survival.

Unfortunately, the percentage of formation of SO_3^{2-} and S^o from the dissociation of thiosulphate and the rate of air flow needed to oxidize SO_3^{2-} to SO_4^{2-} were not measured. Also unmeasured was the conversion of sulphur, produced from thiosulphate dissociation, to sulphate.

It remains, then, that at the low pH values of the mixed liquor (pH 2.10), oxidation of thiosulphate to sulphate by T. thiooxidans as the sole mechanism, as was originally assumed, may not be completely valid.

CHAPTER 7

CONCLUSIONS

Results from the separate investigations conducted into the effects of influent phosphorous and retention times on the oxidation of thiosulphate indicate for both studies that:

(1) Activated sludge, with the addition of Thiobacillus thioxidans can be acclimatized to treat thiosulphate wastes, although the final mixed liquor bears little resemblance to the original activated sludge.

(2) A completely mixed reactor without recycle, using suspended growth can effectively treat thiosulphate in concentrations up to about 984 mg/l.

(3) Low mixed liquor and effluent pH values indicate that the unit is achieving a high percentage of thiosulphate removal. When functioning efficiently at steady state, these values were consistently at pH 2.1. Increasing pH values greater than pH 2.1 signify impending failure.

(4) Solids production is low and the procedure used to determine TSS values proved unsatisfactory. Colloidal particles, possibly of sulphur, were present in the reactor and interfered with the conventional TSS analysis.

(5) Biomass production is low, typical of autotrophic systems, and estimates using the conventional VSS determination were unsatisfatory.

(6) Sludge production for the duration of both studies was insignificant.

(7) Effluent turibidity was found to be a suitable indicator of reactor performance. When operating efficiently at steady state, effluent turbidity values were consistently below 20 NTU. Prior to reactor failure turbidity values increased dramatically and was a good visual indicator of imminent failure.

7.1 Influent Phosphorous Variation Study

Conclusions relating specifically to this study are:

(1) Little difference was noted in the effluent characteristics between the reactors as a result of the varying influent phosphorous concentrations when the reactors were functioning efficiently at steady state.

(2) Phosphorous requirements were low. An influent phosphorous concentration of 2.96 mg/l PO_4-P was sufficient for 99 percent thiosulphate removal, with a retention of 5 days and operations conducted at room temperature.

(3) Polythionate production was the lowest for the lowest influent phosphorous concentration.

7.2 Retention Time Variation Study

Conclusions relating specifically to this study are:

(1) Retention times of 4, 3 and 2 days show little difference in all

aspects of effluent characteristics. Influent phosphorous was 9.80 mg/l PO_4-P with operations conducted at room temperature.

(2) A retention time of 1 day was the lowest time capable of achieving satisfactory thiosulphate removal without reactor failure. Influent phosphorous was 9.80 mg/l PO_4-P with operations conducted at room temperature.

(3) A retention time of 1/2 day proved insufficient failing after 10 days of operation.

(4) The washout retention time is between 1/4 and 1/2 day, at room temperature.

CHAPTER 8

RECOMMENDATIONS

The oxidation of thiosulphate has been extensively investigated on a microbiological basis, and the results have been applied successfully to the waste water engineering fields, especially to the oxidation of thiosulphate (and polythionates) originating from various base metal mining operations.

Engineering developments of microbiological studies have progressed to the recommended method of thiosulphate oxidation - use of the rotating biological contractor or biodisc. Results with the fixed film growth reactors have been successful both with laboratory scale studies and pilot plant operations in the field.

For suspended growth systems, however, such as the complete mix reactors without recycle used for this report, evidence indicates that due to the low biomass concentration removal rates are not as great as for the fixed film reactors.

To establish the capabilities and limitations of suspended growth systems then, the following is recommended:

(1) Investigation of high and low temperatures on solids retention time.

(2) Determination of the maximum concentration of thiosulphate capable of treatment under optimum conditions of nutrients, temperature and retention time.

(3) Feasibility of low temperature operation, representative of Canadian winters, and the maximum concentration of thiosulphate capable of treatment at these low temperatures.

(4) Investigation into the application of chemical oxidants for the chemical oxidation of thiosulphate.

(5) Investigation of the effects of heavy metals, at typical concentrations found in the mining effluents, on the biological oxidation of thiosulphate and determination of the maximum tolerable concentration of these heavy metals.

A further recommendation for future work, not related directly to that for suspended growth systems mentioned above, centres primarily on seeking a clearer understanding of the exact nature of thiosulphate oxidation. That is, determining whether what is generally regarded solely as a biological oxidation mechanism is not in fact either, solely, a chemical oxidation, or a combination, in whatever proportions, of both.

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